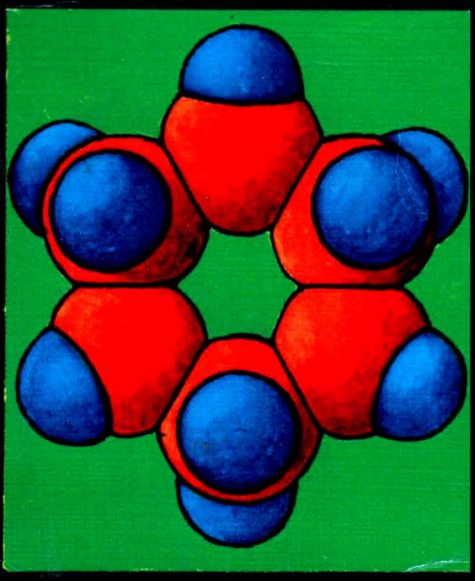
ORGANIC

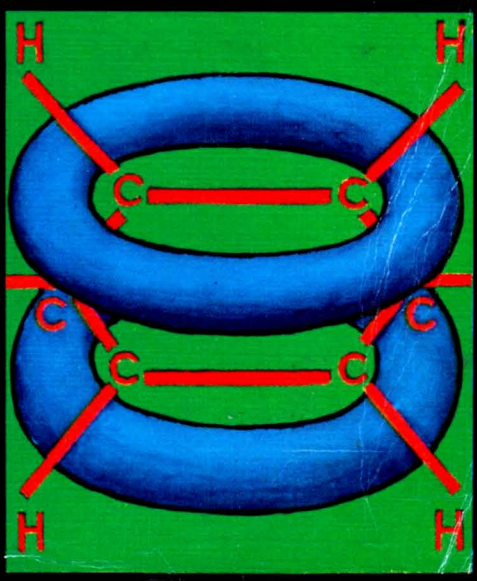
# CHEMISTRY

TEXTBOOK FOR SCHOOLS

L.A.Tsvetkov

The Theory of Chemical Structure of Organic Compounds.
Saturated Hydrocarbons. Unsaturated Hydrocarbons.
Aromatic Hydrocarbons. Natural Sources of Hydrocarbons.
Alcohols and Phenols. Aldehydes and Carboxylic Acids.
Esters. Fats.
Carbohydrates. Amines. Aminoacids. Proteins.



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Л. А. Цветков
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# CHEMISTRY

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L.A.Tsvetkov

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# Introduction

The Subject Matter of Organic Chemistry. While studying inorganic chemistry, we became acquainted with substances of most varied composition, but we never came across one element that had to be present in every compound. Organic compounds always contain carbon in addition to other elements. The study of carbon compounds, their structure, and chemical conversions, are the subject matter of organic chemistry.

Inorganic and Organic Substances. In addition to carbon, organic compounds usually contain hydrogen, oxygen, and nitrogen; less frequently organic compounds contain sulphur, phosphorus, the halogens, or other elements. Several million organic compounds are known at the present time, and their number is still increasing. The number of inorganic compounds is much smaller. Of all the chemical elements, only carbon can form this multitude of compounds.

We deal with organic substances every day. They are contained in every plant and animal organism, and in food (bread, meat, vegetables, etc.), they are used for the manufacture of our clothes (textiles, leather), they are fuels, we use them as medicines, dyes, weed-killers, insecticides, and so on.

Almost all organic substances are combustible and easily decompose at high temperatures. Organic compounds can be identified by the formation of carbon dioxide during burning or by charring at high temperatures.

There is no distinct borderline between organic and inorganic substances. Carbon oxides, carbonic acid, its salts, and some other compounds that contain carbon might be expected to be organic substances. But their properties are close to those of inorganic compounds with similar structure and therefore, they are studied by inorganic chemistry. We know from biology that inorganic substances can form organic compounds, while organic compounds may be converted into inorganic ones.

Organic Chemistry as a Separate Science. Man has dealt with organic substances from prehistoric times. The production of alcohol by fermenting fruit juices and the production of vinegar by fermenting alcoholic liquids have been known for thousands of years. Our forefathers also used natural dyes, cane sugar, vegetable oils, animal fats, etc. But a separate science of carbon compounds only came into being in the first half of the last century. Until then, all the substances were classified by their origin into three groups: mineral, vegetable, and animal, and each group was studied separately.

As the methods of chemical assay gradually improved, it was established that substances of plant and animal origin contained carbon. The Swedish chemist Berzelius (1807) suggested that substances derived from organisms be called organic, and that the science studying them be called organic chemistry.

But Berzelius and his contemporaries believed that organic substances were quite different from inorganic ones, and that they could not be obtained in the laboratory like inorganic compounds. They believed that organic substances could only be formed by living organisms through the agency of a "vital force". This doctrine, known as vitalism (from Latin *vita*, life), was erroneous because it was based on the belief in an immaterial and supernatural force. According to

vitalism an organic substance could not be obtained from inorganic compounds. This doctrine slowed down the development of science, but it could not stop the onward march of the scientific study of nature.

Wöhler, a disciple of Berzelius, synthesized an organic substance from inorganic compounds in 1828. This substance was urea, and in 1845 the German chemist Kolbe prepared acetic acid. In 1854 the French chemist Berthelot synthesized fats, and in 1861 the Russian scientist Butlerov synthesized a simple sugar. The fact that organic substances, which were formerly produced only by living organisms could now be formed artificially was a devastating blow to the doctrine of the "vital force".

Advances in Modern Organic Chemistry and Its Role in the Study of the World and in the Economy. Now man can synthesize not only naturally occurring substances, but also organic compounds that are not found in nature, e.g. plastics, rubbers, dyes, explosives, and medicines.

The number of synthesized substances now exceeds the number of naturally occurring substances, and new organic substances are being created every year. Organic chemistry now approaches a symbolic land-mark in that now the most complicated organic substance, protein, is being synthesized. Comparatively simple proteins such as hormones and enzymes have already been synthesized. We believe that the time will soon come when more complicated proteins will also be made artificially.

The term "organic substance" has expanded in meaning. It now implies both substances contained in living organisms and, moreover, substances that have nothing to do with the living world, but which have been created by man. The term "organic" has come down to us from the old times and so we use it to designate the whole group of substances containing carbon.

Modern organic chemistry studies processes occurring in the cells of living organisms at the molecular level and mechanisms, which are the basis of life. Engels wrote about the historical role of chemical investigations:

"Physics had to leave out, or was able to do so, the living organic body; chemistry finds only in the investigation of organic compounds the real clue to the true nature of the most important bodies, and, on the other hand, it synthesizes bodies, which only occur in organic nature. Here chemistry leads to organic life, and it has gone far enough to assure us that it alone will explain to us the dialectical transition to the organism."

The study of the chemistry of organic substances thus broadens our knowledge of nature. By showing the connections between substances, and by studying a great number of substances including simple inorganic and most complicated organic compounds organic chemistry reveals the development of nature, and helps us understand the processes occurring in nature and the laws governing them. Organic chemistry thus makes an important contribution to our scientific and materialistic understanding of the world.

Advances in organic chemistry are widely used in modern industry. Natural substances are converted into a wide variety of synthetic products for various industries, agriculture, medicine, and everyday life.

All these aspects of organic chemistry will become clear to you as we shall progress in the study of this science.

# 1 Chemical Structure of Organic Compounds

## 1.1 Precursors of the Theory of Structure

When we studied inorganic chemistry we always used the Periodic Law and the Periodic System of chemical elements. In studying organic chemistry we shall likewise use the theory of chemical structure.

The basic principles of the theory of chemical structure were developed in the 60s of the past century.

The main objective of organic chemistry in the first half of the 19th century was the study of the composition and properties of natural compounds and working out rational methods for using them in practice. The development of industry and trade, and the growth of towns and cities imposed new requirements on organic chemistry. The textile industry needed various dyestuffs, the food industry needed better methods of processing the country products, the illumination of the cities required new approach to the utilization of natural materials, the growing population needed medicines.

But the development of organic chemistry was slow because of the inadequate development of the theory. New phenomena discovered during investigations of organic substances required theoretical explanations and systematization. But the theory of the time could not keep pace with practical developments. Organic chemistry had to produce new substances, but the theory could not indicate how to synthesize them.

Let us consider some facts to illustrate the gap between the requirements of practical organic chemistry and the state of the theory in those days.

We know that carbon reacts with hydrogen to yield many compounds known as hydrocarbons. Natural gas, for example, contains ethane $C_2H_6$, propane $C_3H_8$, butane $C_4H_{10}$, etc. in addition to the simplest hydrocarbon methane $CH_4$. Thermal decomposition of coal gives benzene $C_6H_6$, toluene $C_7H_8$, etc. Many hydrocarbons are contained in petroleum. A question arises, why the two elements can form so many compounds? And another question: why does the number of organic compounds exceed so greatly the number of inorganic compounds?

Consider in more detail the composition of hydrocarbons, e.g. those contained in natural gas. Carbon is a tetravalent element. But it remains tetravalent only in methane $CH_4$, while in ethane $C_2H_6$ carbon appears to be trivalent, and in propane $C_3H_8$ its valency should be a fractional number. What, in fact, is the valency of carbon in organic compounds?

Another example. We know from biology that the molecular formula of glucose is $C_6H_{12}O_6$. But fructose (the sugar extracted from fruits, honey) has

the same formula. While studying inorganic chemistry we never dealt with different compounds that had the same molecular composition. But during the early 19th century many such phenomena were discovered. These substances were discovered to have the same composition but different properties and Berzelius gave them the name isomers. The cause of isomerism needed theoretical explanation.

Chemical symbols were not used in any systematic way either. Scientists were mainly interested in the conversion of one substance into another and they wrote chemical formulas so that they could explain the chemical properties of a substance. The same substance was therefore often given different formulas, depending on the particular conversion. Many formulas, sometimes very cumbersome, were thus in use, and investigators often failed to understand one another.

Wöhler wrote in 1835 to Berzelius that organic chemistry could drive someone mad. He likened organic chemistry to a thick wood full of wonderful things, into which one can hardly venture to enter without leaving all hope of return.

We have mentioned only a few of the many problems that required the theoretical explanation. However, investigators of that time faced many other complicated problems.

? 1. Give examples to illustrate the contradictions between the facts then known and the theory in the middle of the last century.

△ 2. What valency should be assigned to carbon in (a) benzene, (b) toluene (see the formulas above) if we follow our usual concept of valency?

## 1.2 The Theory of Chemical Structure

The principles of the new theory were formulated in 1861 by Alexander Butlerov, a professor at the University of Kazan. The ideas of the atomic theory were spreading rather rapidly at that time. The concepts of the atom and molecule, which had not been strictly differentiated till that time, were strictly defined in 1860 at the international congress of chemists. However, investigators did not attribute much importance to the structure of the molecule and believed that the arrangement of atoms in the molecule could not be studied by chemical methods. Some scientists did not even believe that atoms and molecules existed at all.

Butlerov maintained that atoms and molecules existed and concluded that the atoms in a molecule are not arranged at random but in a certain order which could be determined by chemical methods and described by the formula. Butlerov formulated the main idea of his theory as follows: "The chemical nature of a composite particle depends on the nature of the elementary particles, which make up a given substance, and on the number of such particles and their chemical structure". If we word it today in more common terms, we would say that the chemical properties of a molecule depend on the properties of the atoms that compose this molecule, on the number of atoms, and on the chemical structure of the molecule.

According to Butlerov, the chemical structure is the order in which the atoms

Alexander Mikhailovich BUTLEROV
(1828–1886)

A Professor at Kazan and later at St. Petersburg University, academician. He created the theory of chemical structure which laid the foundation for modern organic chemistry. He predicted some new compounds using his theory and was the first to synthesize them. He discovered the polymerization reaction of unsaturated hydrocarbons to show the ways of synthesis of high-molecular compounds. His ideas concerning the hydration of ethylene are now used in the manufacture of ethyl alcohol. He was the first to synthesize sugars (hexoses).

are connected together in the molecule, and their influence on each other. The atoms, Butlerov maintained, combined in molecules in agreement with their atomicity (valency).

Taking examples from inorganic chemistry, we can see that atoms affect each other as they combine into a molecule. For example, when hydrogen and oxygen produce water, they change their initial properties so much that the hydrogen in the water can no longer burn, while the oxygen can no longer support burning. Thus water has neither the properties of hydrogen nor of oxygen.

Consider the following hydrogen compounds: HCl, $H_2O$, and $NH_3$. The hydrogen behaves differently in each of these compounds. It can be easily replaced by many metals when it exists as HCl, while it can only be replaced from water by very active metals. It is even more difficult to replace hydrogen from ammonia. The atoms connected to the hydrogen atoms in these molecules have different effects on them.

Compare the strength of the acids $H_2CO_3$, $HPO_3$, and $H_2SO_4$. It is easy to note that the atoms of carbon, phosphorus, and sulphur have different effects on the hydrogen as well.

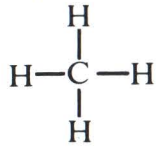
The essence of the theory of chemical structure can, according to Butlerov, be formulated as follows:

● 1. Atoms in molecules are not randomly arranged but are connected together in a certain order in accordance with their valency.

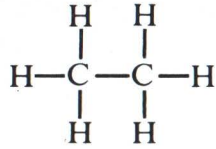
2. The properties of a substance depend not only on the type and number of atoms that compose the molecule, but also on the way they are connected together in the molecule, and on the manner in which they affect each other.

Consider the first principle using the hydrocarbons. In what order are the atoms connected together in the molecule of the simplest hydrocarbon, methane? We already know that each hydrogen atom in methane is connected to the carbon atom. It is easy to understand that it cannot be otherwise. If, for

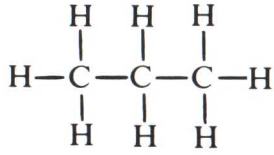
example, we assume that two hydrogen atoms are connected with one another, they exhaust their valencies and so cannot be connected to any other atoms. If we use a dash to designate valency, the atoms in the methane molecule will be arranged as follows

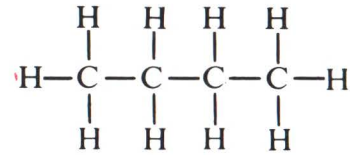


If we want to arrange all the hydrogen and carbon atoms in a molecule of ethane $C_2H_6$, the carbon atoms must be connected to each other. They spend one valency unit each to form a bond between them, and to leave three vacant valency units, by which they can attach six hydrogen atoms



The atoms in molecules of propane $C_3H_8$ and butane $C_4H_{10}$ are connected together as follows:





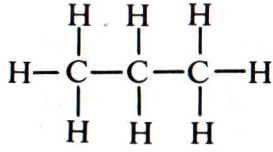
Once we know the structure of hydrocarbons, we can now answer some of the questions that troubled chemists of the last century.

How can the huge variety of carbon compounds be explained? The reason is that carbon atoms can join together to form chains.

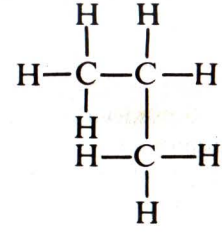
Does the valency of the elements change in these compounds? No, it does not. The carbon atom remains tetravalent in all compounds.

Chemical formulas showing the arrangement of atoms in molecules are called *structural formulas.*

It should be remembered that the structural formula only shows the order in which the atoms are connected but it does not show how the atoms are arranged in space. The structural formula of propane can therefore be presented as either



or



The order in which the atoms follow each other in both formulas is the same.

Structural formulas of substances are often given in an abbreviated form, e. g. $CH_3—CH_2—CH_3$, where the dash shows the bond between each carbon atom but does not show the bond between the carbon and hydrogen atoms.

? 1. What are the main principles of the theory of chemical structure? Give examples to illustrate your understanding of the theory with respect to the order of connections between the atoms in molecules.

△ 2. Give examples from inorganic chemistry to show that atoms affect each other as they combine into molecules and that their initial properties change.

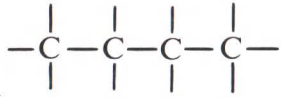
3. Write out structural formulas of the following hydrocarbons: (a) pentane $C_5H_{12}$, (b) hexane $C_6H_{14}$ following the patterns given above.

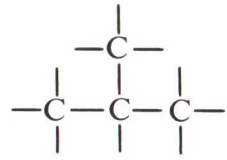
## 1.3 Isomerism

Let us now discuss the effect that the arrangement of the atoms in a molecule has on the properties of substances.

Consider first some historical facts. Butlerov studied the structure of hydrocarbon molecules and concluded that, beginning with butane, atoms of the same molecule can be combined in a different way.

The atoms in butane $C_4H_{10}$, for example, may be arranged either as a straight chain or as a chain with a branch

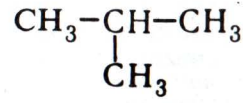




In the first case each terminal carbon atom is connected to one other carbon atom while the two middle atoms are connected to two carbon atoms. In the second case there is a carbon atom which is connected to three carbon atoms. According to the theory of chemical structure, different connection between atoms may only occur in different substances, although the qualitative and quantitative composition of their molecules is the same. If the theory is correct, there should be two butanes which differ in their structure and properties. Only one butane was known at the time of Butlerov, and so he undertook an attempt to synthesize a butane with a different structure. The substance that he obtained in his experiment had the same composition $C_4H_{10}$, but its properties were different. The boiling point of the new substance was lower, for example. As distinct from butane, the new compound was called isobutane (from Greek *isos*, equal).

$CH_3—CH_2—CH_2—CH_3$

Butane
(b.p. −0.5° C)



Isobutane
(b.p. −11.7° C)

Butlerov studied the structure of pentane $C_5H_{12}$ and concluded that three hydrocarbons with this composition might exist:

$CH_3-CH_2-CH_2-CH_2-CH_3$ (b.p. 36.2° C)

$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_2-CH_3$ (b.p. 28° C)

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

(b.p. 9.5° C)

All the three substances were synthesized.

As the number of carbon atoms in the molecule increases, the number of substances with the same composition increases rapidly. According to the theory, 75 hydrocarbons with the composition $C_{10}H_{22}$ may exist, 1858 with the composition of $C_{14}H_{30}$, etc. The phenomenon of isomerism, i.e. existence of several different substances with the same composition, has been known for a long time. But it was only with the formulation of the theory of chemical structure that isomerism was explained. We can now define isomers as follows.

● Substances having the same composition (the same molecular formula) but different chemical structures and different properties are called isomers.

The evidence supporting the theory of chemical structure continued to increase and it was gradually acknowledged universally. More than a hundred years have passed since then and the theory of chemical structure has become a fundamental theory in organic chemistry. The theory was first formulated to explain the structure of organic compounds, but later it spread into chemistry in general because it is equally true for inorganic compounds with molecular structure (e.g. water, ammonia, nitric acid, sulphuric acid). The scientific importance of this theory consisted in that it broadened our knowledge of substance, deepened our understanding of the inner structure of molecules, explained facts that had been accumulated in chemistry, made it possible to predict new substances, and indicated how to synthesize them. Organic chemistry and the chemical industry owe their development largely to the theory of chemical structure.

While creating his theory of chemical structure, Butlerov used the achievements of his predecessors. The concept of valency of elements was the starting point for his theory. This concept was introduced into science by the English chemist Frankland (in the early 50's of the 19th century). The German scientist Kekulé established that carbon was tetravalent, a fact which is especially important for organic chemistry. Kekulé and Couper suggested that carbon atoms might combine with one another to form chains, but these were all separate ideas. Butlerov created a whole theory of chemical structure which explained how the properties of a substance depend on its structure, and indicated how to establish the structure of a substance and to predict new substances.

Butlerov worked out his theory and proved it experimentally, but he never believed that his theory was absolute and that it could not be further developed. He foresaw that his theory would be modified by resolving contradictions between theory and newly discovered facts.

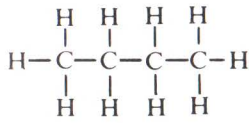
Indeed, the theory of chemical structure has not remained unchanged and it has been developed in two main and closely related directions.

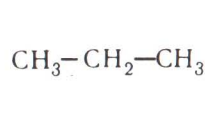
The first was suggested by Butlerov himself. He believed that in the future, chemistry would establish not only the order of atoms in molecules, but also their spatial arrangement. The study of spatial structure of molecules is called *stereochemistry*. This new branch of chemistry began to develop during the 1880's. It helped to explain new otherwise inexplicable facts.

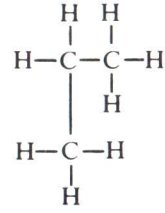
The second development was the application of the theory of *electron structure of atoms* to organic chemistry. This theory originated in the 20th century and explained the nature of chemical bonds between atoms, their mutual influence and the chemical properties of substances.

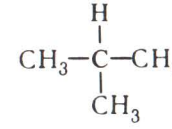
? 1. Give examples to illustrate the dependence of properties of substances on their chemical structure.

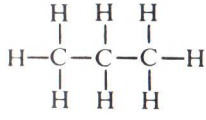
△ 2. How many substances are described by the following seven structural formulas?

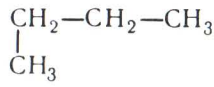


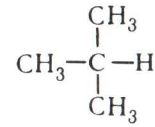












3. Draw structural formulas for the molecules of (a) hydrogen sulphide, (b) carbon dioxide, and (c) phosphoric acid.

4. Which scientific ideas were the precursors of the theory of chemical structure? Who were the authors to these ideas?

## 1.4 The Electron Nature of Chemical Bonds in Organic Substances

We shall often refer to the structure of atoms and the electron nature of chemical bonds in molecules during our study of organic chemistry. Let us recollect what we know already about this subject. First consider the structure of some chemical elements (Fig. 1).

The *hydrogen* atom consists of nucleus and one *s* electron, which moves around the nucleus to create a negatively charged spherical electron cloud. The greatest density of this cloud (the highest probability of finding the electron) is

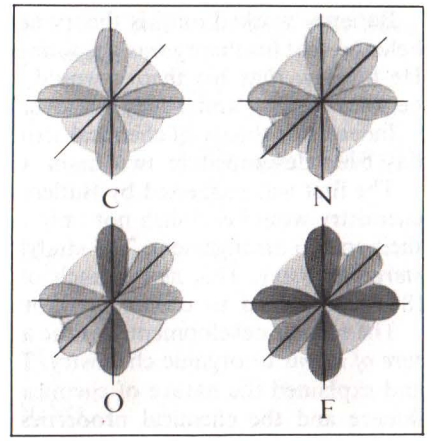



Fig. 1. Electron structure of some elements of the second period (the inner two-electron layer is not shown)

at a distance of 0.053 nm from the nucleus.*

The *helium* atom has two *s* electrons. They move around the nucleus to form a common electron cloud (also spherical). The electrons are said to be paired.**

Show schematically the structure of atoms of the elements with the atomic numbers 3, 4, and 5, remembering that the third electron in the lithium atom cannot occupy the same orbital as the two *s* electrons and so it begins a new layer in the electron shell of the atom.

The inner layer of the *carbon* atom also contains two *s* electrons, while its outer layer contains two paired *s* electrons and two *p* electrons. As distinct from spheres of *s* electrons, the clouds of the *p* electrons are dumb-bell shaped. The electric charges of the *p* electron clouds have the same signs, and the clouds tend to move as far apart as possible. This accounts for the perpendicular arrangement of the dumb-bell clouds of *p* electrons in the carbon atom.

A third *p* electron appears in the outer layer of the *nitrogen* atom. Its cloud does not coincide with either of the other two *p* electrons since it is perpendicular to the cloud of the former two *p* electrons.

The *oxygen* atom has four *p* electrons. Every mutually perpendicular direction in space is already occupied, and so the fourth *p* electron becomes paired with one of the other *p* electrons. The outer layer of the oxygen atom has two paired *s* electrons and two paired *p* electrons and two unpaired *p* electrons.

It is now easy to predict that the fifth *p* electron of the *fluorine* atom will be paired with one of the remaining free *p* electrons. Only one unpaired *p* electron now remains in the atom. The outer layer of the other halogens has the same structure, but this will be discussed later.

In the *neon* atom (like in those of the other noble gases) all six *p* electrons of its outer layer are paired to account for the chemical inertness of the gas.

Of the two main types of chemical bonds, viz., ionic and covalent, the *covalent bond* is the more characteristic of organic compounds.

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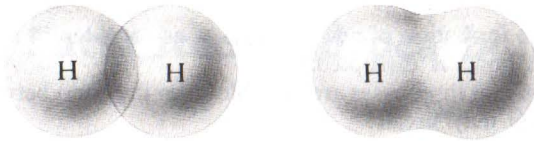
* 1 nanometer (nm) is equal to $10^{-9}$ m.

** Two electrons with different spins can occupy one orbital. (See physics course.)




*a* *b*

Fig. 2. Overlapping of electron clouds in hydrogen atoms (a) and formation of a two-electron molecular cloud (b)

When two atoms approach one another during a chemical reaction, the electron cloud of one atom is attracted by the nucleus of the other atom, and the electron cloud of the other atom by the nucleus of the first atom. The clouds thus become overlapped. The atoms cannot approach each other closer because of the mutual repulsion of the positively charged atomic nuclei. The two electron clouds form a single two-electron cloud, which is common to both atoms. The highest electron density is found in the space between the two nuclei (Fig. 2). The motion of the electrons in the field of the two nuclei and the higher electron density in the space between them increase the attraction force in the molecule and so energy is liberated. The formed molecule has a lower energy and is therefore more stable compared with the initial atoms.

● The greater the extent to which the electron clouds overlap as the two atoms combine, the greater the amount of energy is liberated, and the stronger the chemical bond.

The pattern of formation of covalent bonds changes slightly depending on the reacting atoms. If atoms of one element combine, the region where the electron clouds overlap (the region of the highest electron density) is located symmetrically between the nuclei of the atoms, and the bond thus formed is nonpolar.

If a covalent bond is established between atoms of different elements, e. g. during formation of hydrogen chloride, the overlap region occurs closer to the more electronegative atom. The probability of finding electrons (that form the chemical bond) becomes higher in the vicinity of one nucleus. The other atom becomes deficient of electrons and thus becomes partly positively charged (due to the positive charge of the nucleus). The atom at which electrons are in excess (compared with the charge of the nucleus) becomes partly negative. Thus the resultant covalent bond is polar. It should however be remembered that these charges are only partial because the electrons do not reside around one atom (as happens in an ionic bond) but are only closer to one atom. Partial charges are usually designated as $\delta+$ and $\delta-$. The distribution of electron density and the character of bond in the molecule of hydrogen chloride can be described as $H^{\delta+}—Cl^{\delta-}$. The displacement of the electron density in the chemical bond is sometimes designated as $H \rightarrow Cl$.

Using these graphic methods, indicate the shift of the electron density in the covalent bond C—Cl. What is the distribution of partial charges in these atoms?

We have discussed the formation of covalent bonds between atoms. But a chemical reaction actually consists of two opposite processes: the destruction

of bonds and the formation of new bonds. Let us consider, in a general form, how a covalent bond is disrupted.

It is easy to see that three cases are possible when the bond between atoms (or groups of atoms) may break:

$$A|:B \rightarrow A^+ + B^-;\ A:|B \rightarrow A^- + B^+;\ A\,\dot{|}\,\dot{|}\,B \rightarrow A^{\cdot} + B^{\cdot}$$

The bonds in the first and second cases break so that the electron pair responsible for the chemical bond remains at one part of the molecule (an asymmetrically broken bond). The valency electron is completely transferred from one atom to the other to make one particle a positively charged ion and the other particle a negatively charged ion.

In the third case, the bond breaks down by dividing the electron pair (symmetrical break down). The molecule thus falls into neutral particles, each having one unpaired electron.

● Particles with unpaired electrons are called free radicals. Free radicals are usually very unstable and exceedingly reactive. They soon react to form stable molecules. We can thus conclude that covalent bonds may break with the formation of ions and free radicals.

The mechanism by which a covalent bond is broken in a given reaction depends on the nature of the atoms and the reaction conditions. We shall further discuss this problem in more detail.

---

? 1. Draw the structure of outer electron shells of the atoms of (a) carbon, (b) oxygen and (c) nitrogen. Without consulting the picture in the textbook, show *s* and *p* electrons in the atoms.

△ 2. Draw the structure of a water molecule. Show the overlapping of electron clouds of the oxygen atom with the clouds of the hydrogen atoms.

3. Using the molecule of hydrogen bromide as an example, show how a covalent bond breaks to form (a) ions and (b) free radicals. From what you know from the course of inorganic chemistry, decide if both mechanisms can be realized in reactions between inorganic compounds.

4. Show schematically the break down of one of the C—H bonds in the methane molecule with the formation of free radicals. How many electrons are there in the hydrocarbon radical formed?

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# 2 Saturated Hydrocarbons

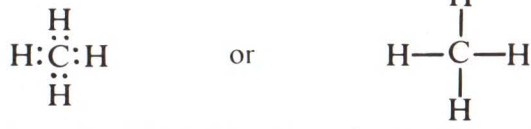
We shall begin the study of organic compounds with the hydrocarbons containing only two chemical elements, viz., carbon and hydrogen. The composition of all hydrocarbons belonging to this large group is expressed conventionally by the formula $C_nH_m$. There are several groups (series) of hydrocarbons. Let us first acquaint with saturated hydrocarbons. Methane, ethane, propane, and butane are representatives of this group.

## 2.1 Structure of Saturated Hydrocarbons

Consider the simplest saturated compound, methane.

Methane and Its Structure. Methane $CH_4$ is a gas without colour or odour; it is twice as light as air (prove this by calculations). Methane is formed in nature during decomposition of plant and animal remains in the absence of oxygen. It often occurs therefore in swamps (marsh gas) and coal mines. Methane is the main component of natural gas, which is used as a fuel in industry and domestically.

The chemical bonds between the hydrogen and carbon atoms in the methane molecule are formed by shared electron pairs, they are covalent bonds. The shell of the hydrogen atoms becomes complete with two electrons, while the shell of the carbon atom contains a full octet of electrons:




When the concept of spatial configuration of molecules was introduced in organic chemistry, it became clear that the methane molecule is tetrahedral rather than planar (as we draw it on paper, see Fig. 3).

Let us consider the spatial configuration of the methane molecule. If we consider a carbon atom, we find a seeming contradiction. The carbon atom has four valency electrons, two of which are paired *s* electrons and they cannot form chemical bonds with hydrogen atoms. The chemical bonds should only be formed by the two unpaired *p* electrons. The molecule of methane should then be $CH_2$ rather than $CH_4$, but this goes against reality. The contradiction can be removed as follows.

When a carbon atom reacts with hydrogen atoms, the *s* electrons in its outer layer become unpaired and one of them occupies the vacancy of the third *p* electron to form a dumb-bell cloud perpendicular to the clouds of the other

two *p* electrons. The atom thus becomes *excited*. All four valency electrons are now unpaired and can form four chemical bonds. But another contradiction now arises: the three *p* electrons must form three mutually perpendicular chemical bonds with the hydrogen atoms, i.e. at an angle of 90°. The fourth hydrogen atom may be attached at any suitable position because the *s* electron cloud is spherical. But chemical bonds formed in this way must have different properties. However, we know that all the C—H bonds in the methane molecule are equivalent and arranged at an angle of 109°28′. The contradiction is resolved by the concept of *hybridization* of electron clouds.

During the formation of chemical bonds, the clouds of all valency electrons of the carbon atom (one *s* and three *p* electrons) become identical (Fig. 4). They form non-symmetric dumb-bells pointing to the vertices of the tetrahedron (a non-symmetric distribution of electron density means that the probability of finding an electron on one side of the nucleus is greater than on the other side).

The angle between the axes of the hybrid electron clouds is 109°28′. The clouds, each having the same charge sign, thus are as far away from each other as possible. Being elongated in the direction of a tetrahedron's vertices, these clouds can be considerably overlapped by the electron clouds of the hydrogen atoms. This results in liberation of energy and the formation of stable and identical chemical bonds (Fig. 5*a*).

Various number of electron clouds may be hybridized. In our case one cloud of the *s* electron and three *p* electron clouds are involved in hybridization. This is called $sp^3$ *hybridization.*

Hence, the tetrahedral configuration of methane molecule depends on the tetrahedral orientation of the four hybrid electron clouds of the carbon atom in the chemical compound.

During the formation of covalent bonds, electrons form clouds for the bonded atoms, and both nuclei appear to be inside the cloud. The structure of

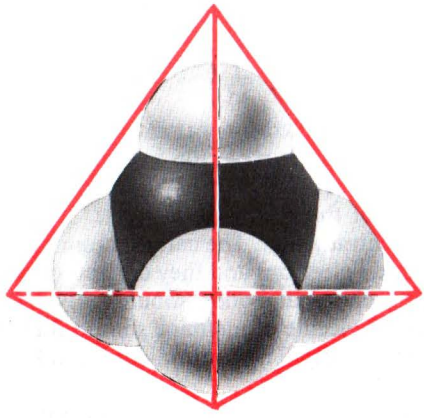


Fig. 3. A model of a methane molecule

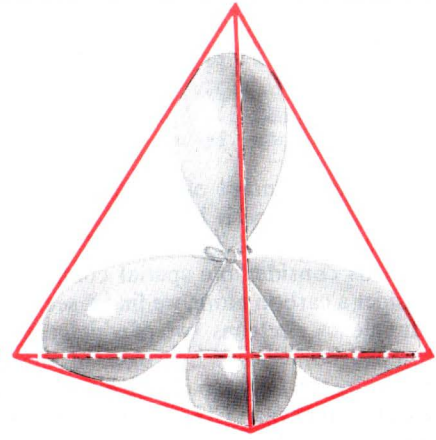


Fig. 4. Hybrid electron clouds of the carbon atom

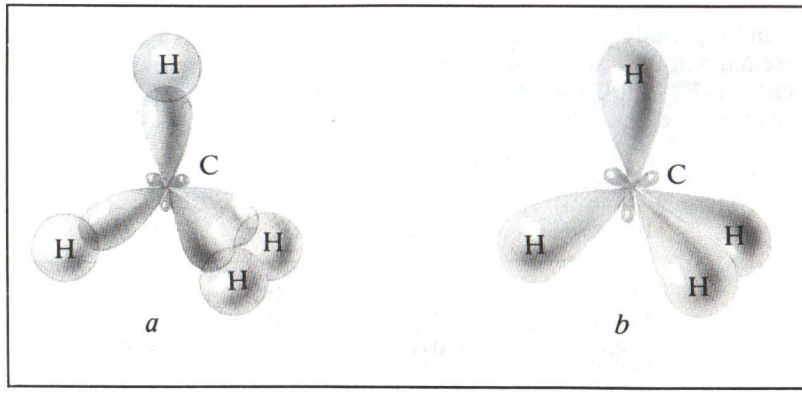



Fig. 5. Covalent chemical bonds in a methane molecule:

*a* – overlapping of electron clouds of the carbon and hydrogen atoms; *b* – formation of common electron clouds of the C–H bonds

methane can thus be shown in another way (Fig. 5*b*).

We shall often use models of molecules. Figure 3 shows a model of the methane molecule in which the relative dimensions of the atoms and the shape of the molecule are approximately correct. In Figure 6, however, the elements of the model are separated from one another by an arbitrary distance. The rods connecting the balls indicate chemical bonds to make the model more vivid. The student can easily see which elements are connected, but no conclusion can be made about the relative dimensions of the atoms or the distances between them.

In fact, when we regard the model shown in Fig. 6, we may conclude that the atoms are far apart. But we know that chemical interaction between atoms can only be realized through direct contact (interaction between outer electrons). In order to make better use of models composed of balls and rods, one must assume that the balls only define the centres of the atoms (their nuclei) rather than atoms themselves, and that the space between the balls is occupied by the electron clouds that form chemical bonds along the rods.

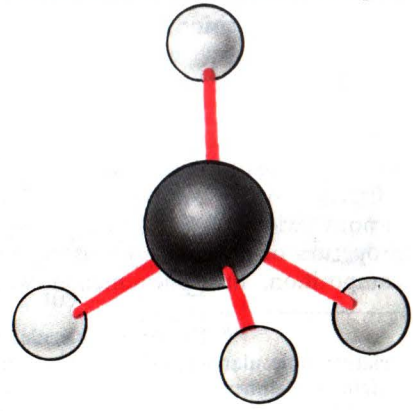


Fig. 6. A model of a methane molecule

The Structure of Hydrocarbons of the Methane Series (the Alkanes). Natural gas, and especially petroleum, contains many hydrocarbons which are similar to methane in their structure and properties. Some of these hydrocarbons are given in Table 2.1. Consider the table and pay attention to the names of the substances and their physical properties.

*Table 2.1*

SATURATED HYDROCARBONS (UNBRANCHED STRUCTURE)

| Hydrocarbon | Formula | M.p., °C | B.p., °C |
|---|---|---|---|
| Methane | $CH_4$ | − 182 | − 162 |
| Ethane | $C_2H_6$ | − 183 | − 89 |
| Propane | $C_3H_8$ | − 187 | − 42 |
| Butane | $C_4H_{10}$ | − 138 | − 0.5 |
| Pentane | $C_5H_{12}$ | − 130 | + 36 |
| Hexane | $C_6H_{14}$ | − 95 | + 69 |
| Heptane | $C_7H_{16}$ | − 91 | + 98 |
| Octane | $C_8H_{18}$ | − 57 | + 126 |
| Nonane | $C_9H_{20}$ | − 54 | + 151 |
| Decane | $C_{10}H_{22}$ | − 30 | + 174 |
| etc. | | | |

The trivial names of the first four substances were given to them long ago, but beginning with pentane, the names are derived from the Greek numbers. In accordance with the system developed by the International Union of Pure and Applied Chemistry (IUPAC system), the ending *-ane* is used to designate saturated hydrocarbons. The data in the table show that as the molecular weights* of the hydrocarbons increase, their melting and boiling points also gradually increase. The first four substances ($C_1$-$C_4$) are gases in normal conditions, while the eleven hydrocarbons that come next ($C_5$-$C_{15}$) are liquids. Hydrocarbons with 16 or more carbon atoms are solids.

If we examine the molecular formulas of the substances in the table, we can see that each substance differs from the previous one by a $CH_2$ group. This is called a methylene group. If we assume that the number of carbon atoms is $n$, then the composition of all these hydrocarbons can be expressed by the general formula $C_nH_{2n+2}$.

All the saturated hydrocarbons are insoluble in water and soluble in organic solvents.

We can give many examples to illustrate how new substances are formed as a result of quantitative changes in the composition. Remember, for example, the difference in the composition and properties of oxygen and ozone, or the various oxides of nitrogen and carbon. If we examine the changes in the properties of hydrocarbons associated with the quantitative changes in their composition, this phenomenon will be especially pronounced and vivid.

* The term 'molecular weight' is commonly used instead of the full 'relative molecular weight'. The short form is used for convenience, though molecular weight is a dimensionless unit, i.e. relative to the weight of the accepted standard.

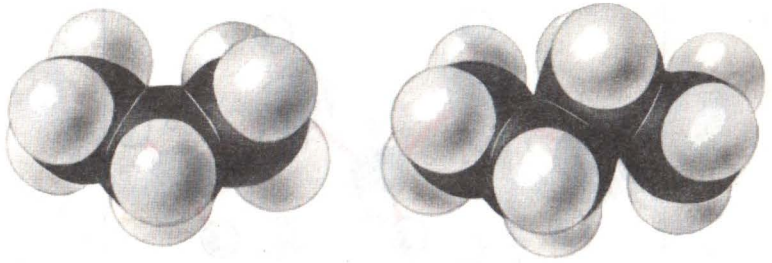


Fig. 7. Models of propane and butane molecules

According to Engels: "Chemistry can be termed the science of the qualitative changes of bodies as a result of changed quantitative composition."

We already discussed the chemical structure of saturated hydrocarbons when we studied the theory of chemical structure worked out by Butlerov. We also got acquainted with the phenomenon of isomerism in the series of hydrocarbons. Differences in the carbon skeleton of molecules account for the existence of different substances with the same composition. We shall now consider in more detail the spatial and electron structure of these compounds.

Figure 7 shows models of propane and butane molecules. It can be seen that the carbon atoms do not form the straight lines that appear in the structural formulas but form zigzags. This structure is due to the tetrahedral orientations of the valency bonds of the carbon atoms.

Let us assume that a carbon atom is attached to another carbon atom. The attached carbon atom has three vacant valency units and they are all directed toward the vertices of a tetrahedron. The next carbon atom can only be attached in one of these directions. The carbon chain thus forms a zigzag (Fig. 8). The angles formed by the covalent bonds between the carbon atoms are 109°28′ (like in the methane molecule). The distance between the adjacent carbon atoms (to be more exact between the centres of the atoms) is 0.154 nm.

The zigzag chain of the carbon atoms can assume various positions in space because the atoms in the molecules can rotate relatively freely about their chemical bonds. Assemble a model of the methane molecule as shown in Fig. 9*a*, and rotate the fourth atom through 180° about the axis that connects it with the third atom. The carbon chain becomes bent (Fig. 9*b*). If we now turn

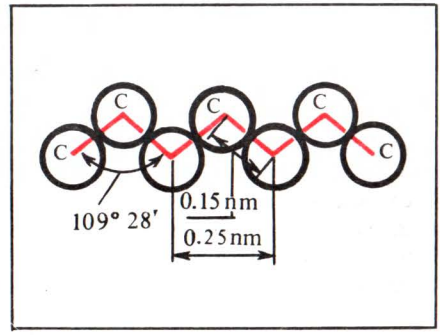



Fig. 8. Zigzag structure of the carbon chain

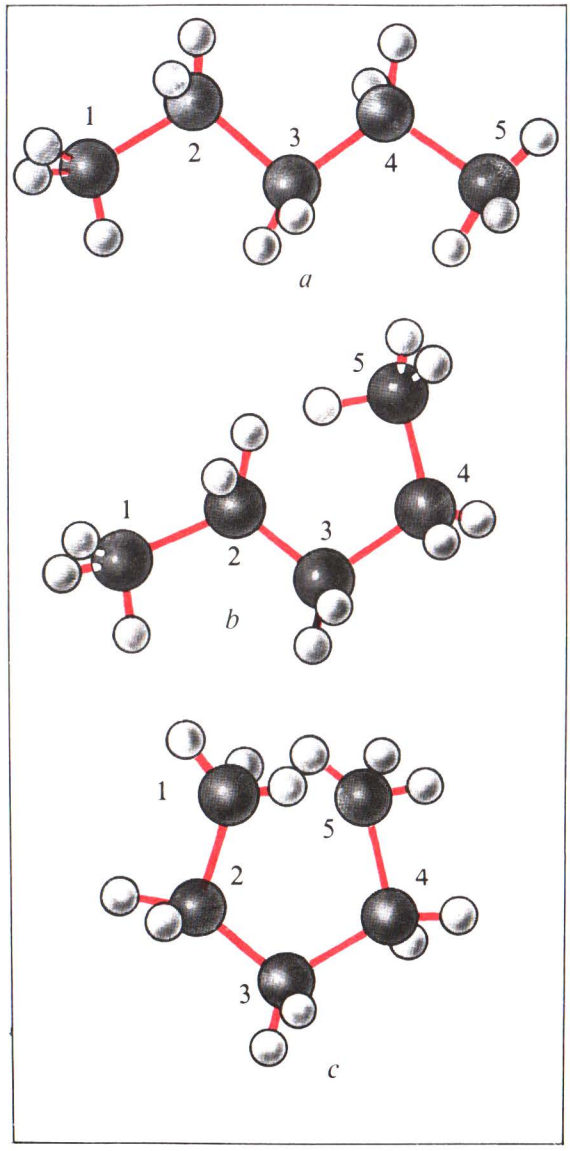



Fig. 9. Models of *n*-pentane molecules

the second carbon atom in the same way, the chain will almost turn into a ring (Fig. 9*c*). This rotation is the form of heat motion (unless there are hindrances). The configuration shown in Fig. 9*a* is the most advantageous energetically, the atoms being as far apart as possible. But all these variations can easily convert into one another, while the chemical structure of the substances (the order in

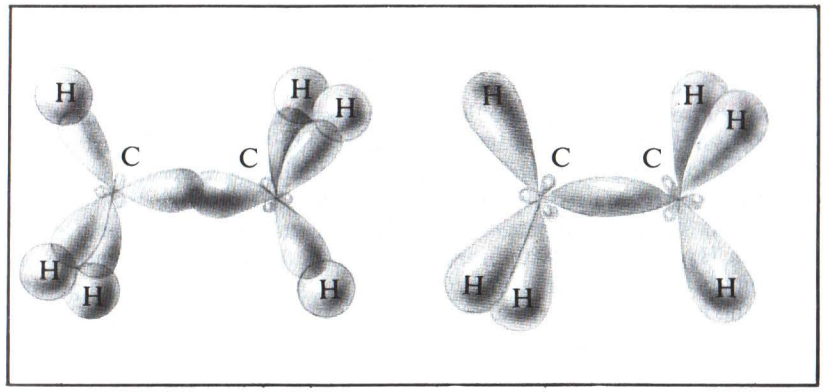



Fig. 10. Formation of the covalent bond between carbon atoms

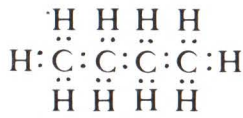
which the atoms are connected in the molecules) remains unchanged and is always expressed by the formula $CH_3—CH_2—CH_2—CH_2—CH_3$.

The remarkable ability of carbon atoms to form long chains is due to their structure and carbon's position in the periodic system.

Carbon comes in the second short period to begin the main subgroup of the group IV of the elements. Its atomic radius is relatively short, and there are four electrons in its outer electron layer. During chemical reactions, it is difficult to remove the four valency electrons from the carbon atom or to recept the same number of electrons from other elements in order to complete the octet. Carbon does not therefore usually form ionic compounds.

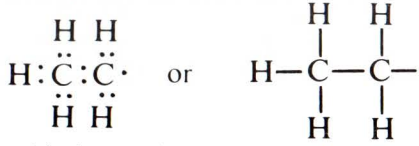
But it can easily form covalent bonds. The ability of the carbon atom to donate electrons is about the same as its ability to accept them during formation of a covalent bond. These bonds can therefore be established between the carbon atoms themselves (Fig. 10).

If we use (as earlier) two dots to designate overlapping electron clouds in covalent bonds, saturated hydrocarbons can be described thus:



These electron formulas do not show the zigzag shape of the molecule.

As the bonds break, the molecules of hydrocarbons can turn into free radicals. If only one hydrogen atom is split off from the molecule, univalent radicals with one unpaired electron are formed:



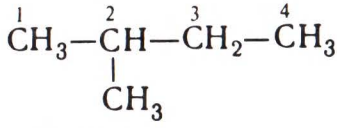

In accordance with the IUPAC system, these radicals derive their names from the corresponding hydrocarbon by changing the ending *-ane* for *-yl*, for example methyl $CH_3—$, ethyl $C_2H_5—$, propyl $C_3H_7—$, etc.

During our study of organic chemistry we shall often deal with radicals, especially with radicals contained in organic substances (in this case they are not called free radicals).

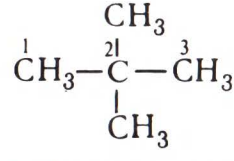
Once we know the structure of hydrocarbons we can explain the dependence of their physical properties on the molecular weight. As the hydrocarbon chain grows, the forces of attraction between the molecules increase, and higher temperatures are required to overcome these forces (to make the substances melt or boil). The physical properties also depend on the spatial structure of the molecules. Hydrocarbons with branched chains boil at lower temperatures than their isomers with linear structures. Compare, for example, the boiling points of butane and isobutane, of normal pentane and its two isomers (see page 14). This phenomenon can be explained as follows. The molecules with the linear structure have closer packing than branched molecules, and more heat is thus required to overcome the intermolecular forces. The more the molecule branches, the weaker the molecules interact, and the lower its boiling point.

Nomenclature. When we deal with isomers, the names we used earlier for the hydrocarbons become insufficiently descriptive. The name pentane, for example, does not specify which isomer is meant. Special names are therefore required to designate isomers.

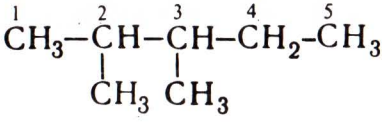
Several naming systems have been proposed, but at the present time scientists have agreed to use the IUPAC system. The names of the linear (normal) hydrocarbons (*methane, ethane, propane, butane, pentane*) are used as the basis for naming other hydrocarbons. To name a particular hydrocarbon with a branched chain, the compound is regarded as the product of the substitution of the hydrogen atoms in the normal hydrocarbon by hydrocarbon radicals. The carbon atoms are numbered consecutively along the longest chain from the end nearest to a branch. The number of the carbon atom to which the substituting group (radical) is attached is then included in the name of the substance. If there are several substituted groups, each is indicated by the corresponding number. If there are substitutions on two carbon atoms equidistant from the ends of the main chain, the carbon atoms are enumerated from the end nearest to the radical with the simpler structure. Consider the following examples



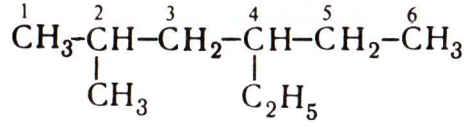
2-Methylbutane



2,2-Dimethylpropane



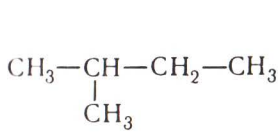
2.3-Dimethylpentane



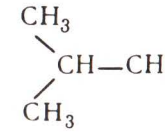
2-Methyl-4-ethylhexane

In order to indicate a hydrocarbon with the normal structure the letter *n* is used, e.g. *n*-butane, *n*-hexane, etc.

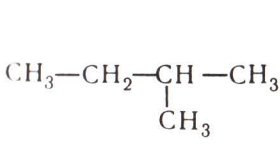
1. Using the electron theory, explain (a) the tetrahedral structure of the methane molecule, (b) the zigzag structure of a carbon chain.
2. Illustrate the changes in physical properties of the substances in the series of saturated hydrocarbons. Draw a graph to illustrate the dependence of a physical property of a hydrocarbon on the number of carbon atoms in its molecule.
3. Write out the molecular formulas for the hydrocarbons of the methane series whose molecules contain (a) 18 carbon atoms, (b) 21 carbon atoms, and (c) 28 carbon atoms.
4. Which of the following hydrocarbons are saturated $C_2H_4$, $C_3H_8$, $C_{10}H_{22}$, $C_6H_6$, $C_{12}H_{24}$?
5. How many substances are described by these formulas

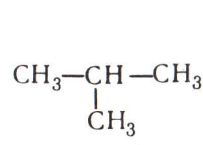


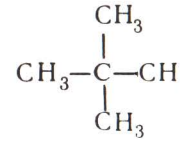


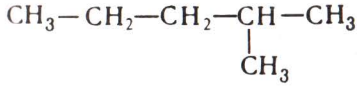


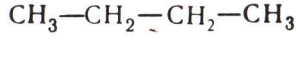
6. Draw structural formulas for all the isomers of *n*-hexane.
7. Identify isomers among the following substances

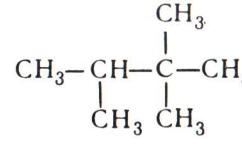




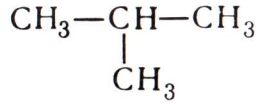




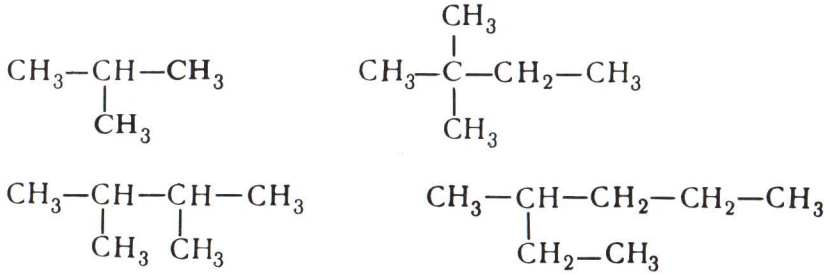




8. Draw electron formulas for (a) *n*-pentane $C_5H_{12}$ and (b) isobutane



9. What sort of particles are known as free radicals? How can their short life be explained?
10. Give names to the following substances using the IUPAC system:



11. Draw structural formulas for (a) 3-ethylheptane, (b) 2,4-dimethylhexane, (c) 2-methyl-3-ethylheptane, (d) 3-methyl-5-ethylheptane.
12. Write down the molecular formula for a substance containing 82.8 per cent carbon and 17.2 per cent hydrogen (by weight). The density of this substance under normal conditions is 2.59 g/litre.

13. A hydrocarbon weighing 8.8 g was burnt to give 26.4 g of carbon dioxide. The density of the substance under normal conditions is 1.96 g/litre. Derive the molecular formula of the hydrocarbon.

Use clay or Plasticine to make a model of (a) propane, (b) all the isomers of pentane as shown in Fig. 7.

## 2.2 Chemical Properties of Saturated Hydrocarbons. Substitution Mechanism

Chemical Properties. Hydrocarbons burn in air evolving a great deal of heat. The combustion of methane can be expressed by the following equation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 880 \text{ kJ}$$

In organic chemistry the equals sign is replaced in equations by an arrow, or two arrows pointing in opposite directions.

By examining the products of methane combustion, it can be shown that methane contains both carbon and hydrogen. Set fire to the gas in a glass cylinder. (Caution!) When the burning stops, you will see droplets of water on the glass walls. Add lime water and shake: the lime water becomes cloudy indicating the presence of carbon dioxide, which was formed by the combustion of the methane. We can thus conclude that the hydrogen and carbon which are required for the formation of water and carbon dioxide were contained in methane.

A mixture of methane and air or oxygen is explosive. The most powerful explosion occurs if one volume of methane is mixed with two volumes of oxygen (see the equation). If we use air instead of oxygen, the most powerful explosion occurs when the methane to air ratio is 1 : 10. Explain why? However, mixtures of methane and oxygen taken in other proportions are also explosive and this is why there is a danger of explosion in coal mines, boiler plants, and places where gas is used. Automatic gas analyzers are used in coal mines and they sound an alarm if gas is present in explosive concentrations in the air. Ventilation systems have now been installed to ensure the safety of workers in coal mines.

The reaction of propane burning can be expressed similarly:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + Q$$

Burning of high-molecular weight hydrocarbons is quite different. Place a piece of paraffin wax (a mixture of solid hydrocarbons) in a porcelain dish and melt it. If we now light it, a great deal of soot will be formed. When gaseous hydrocarbons burn in air they mix well with it and burn completely, but when molten paraffin wax burns, the amount of oxygen is insufficient and free carbon is thus liberated.

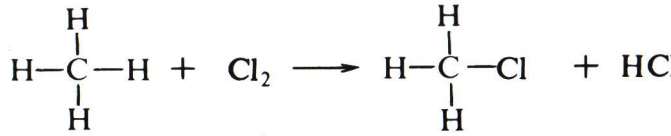
When heated strongly, hydrocarbons are decomposed into simple substances, viz. hydrogen and carbon:

$$CH_4 \rightarrow C + 2H_2 - Q$$

$$C_2H_6 \rightarrow 2C + 3H_2 - Q$$

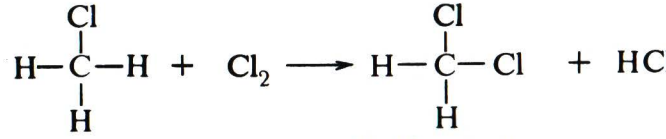
These reactions prove that the molecular formula for the substance is correct: two volumes of hydrogen are evolved when one volume of methane is decomposed and three volumes when one volume of ethane is decomposed (the volume of the solid carbon being disregarded).

The reaction of hydrocarbons with the halogens (with chlorine in particular) is also characteristic. If we expose a mixture of methane and chlorine to diffuse sunlight (direct sunlight causes an explosion), the yellow-green colour of the chlorine gradually fades because of the reaction between the chlorine and methane. The first step in this photochemical reaction is expressed by the equation

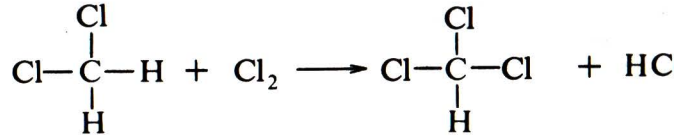



Chloromethane

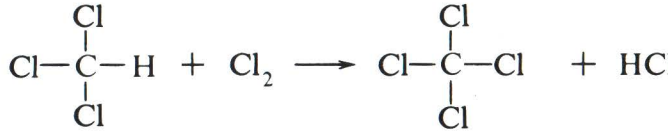
But the reaction normally continues as follows




Dichloromethane




Trichloromethane



Tetrachloromethane
(Chloroform)

The consecutive chain of methane reactions with chlorine can be expressed by the following scheme

$$CH_4 \xrightarrow{+Cl_2} CH_3Cl \xrightarrow{+Cl_2} CH_2Cl_2 \xrightarrow{+Cl_2} CHCl_3 \xrightarrow{+Cl_2} CCl_4$$

Chlorine reacts with the other hydrocarbons in the same way, e.g.

$$CH_3{-}CH_3 + Cl_2 \rightarrow CH_3{-}CH_2Cl + HCl$$

Chloroethane (Ethyl chloride)

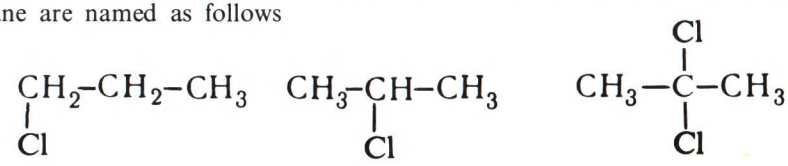
$$CH_3{-}CH_2Cl + Cl_2 \rightarrow CH_3{-}CHCl_2 + HCl$$

1,1-Dichloroethane

The substitution of chlorine for the hydrogen atoms in organic substances is called *chlorination*. Mixture of chlorine derivatives of the corresponding hydrocarbon is usually formed.

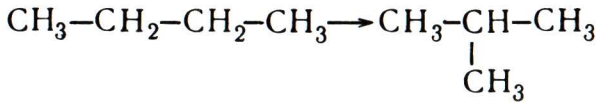
Substitution in organic chemistry differs from the substitution reactions of inorganic chemistry. In the latter the products of substitution reactions are a compound and a simple substance, whereas the products of substitution reactions in organic chemistry are two compounds. What characterises a substitution reaction is the type of changes that occur in the initial organic substance. In our case some atoms were substituted for other atoms.

The position of the halogen atoms in the molecules of chlorine derivatives is described by a number in accordance with the IUPAC system, in fact in the same way as we numbered the hydrocarbon radicals. The chlorine derivatives of propane are named as follows



1-Chloropropane 2-Chloropropane 2,2-Dichloropropane

If hydrocarbons contain four or more carbon atoms they can be *isomerized*. Butane, for example, when heated in the presence of aluminium chloride, is converted into isobutane



Explain, why hydrocarbons having less than four carbon atoms cannot be isomerized.

When the chemical properties of a substance are described, its reactions with acids, alkalis, and oxidants are usually specified. These reagents do not react with the hydrocarbons we are describing in normal conditions. If methane is passed through, for example, a solution of potassium permanganate $KMnO_4$ (a strong oxidant), the violet colour of the permanganate does not change. This indicates that its solution does not oxidize methane.

The alkanes do not participate in the combination reactions with other substances, because their carbon atoms have already exhausted their valencies: they have no more electrons which they can use to establish additional covalent bonds. These compounds are saturated by the hydrogen atoms, hence their name *saturated*. They are also called the *alkanes* or *paraffins* (from Latin *parum* too little + *affinis* affinity) because of their chemical inactivity.

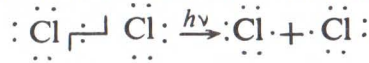
Saturated hydrocarbons thus have similar chemical properties because of their similar chemical structure. But similarity does not mean identity. Remember the differences in behaviour that we discussed above.

● Substances similar in structure and chemical properties though differing in composition of their molecules by one or more $CH_2$ groups are called homologues and form a homologous series.

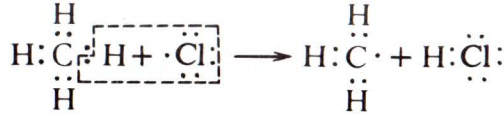
ethane, propane, butane, etc.) are homologues and form the homologous series of saturated hydrocarbons, or paraffins (alkanes). The methylene group $CH_2$ is called the *homologous difference*.

The Mechanism of Substitution. The equations describing the reactions of the alkanes with chlorine are only simple ones, for the reactions are actually much more complicated, and are realized through the formation of intermediate free radicals. Consider the reaction of methane chlorination by the way of illustration.

When the light energy is absorbed by the mixture of methane and chlorine (or if the mixture is heated) the chlorine molecule decomposes into individual atoms (chlorine-chlorine bonds are weaker than the bonds in methane):

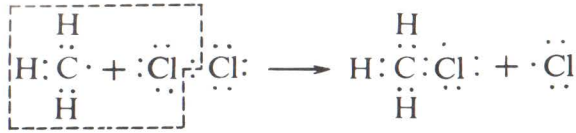


Each chlorine atom has seven electrons in its outer layer. One of them is unpaired. This chlorine atom is actually a free radical. Its energy is high and this accounts for its high chemical activity. When the chlorine atom nears the molecule of methane, its electron interacts with the electron cloud of the hydrogen atom to establish a covalent bond and the molecule of hydrogen chloride is thus formed:

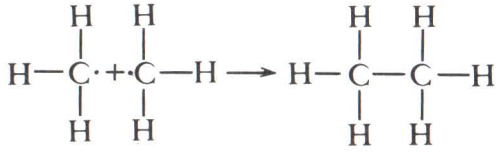


The methane molecule is thus converted into a particle with one unpaired electron. This methyl radical remains in the free state for only about $8 \times 10^{-3}$ second and reacts with another chlorine molecule breaking the chlorine-

chlorine bond. A molecule of chloromethane (methyl chloride) is thus formed



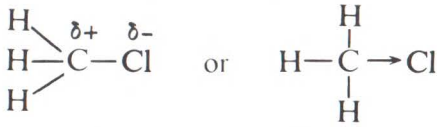
The chlorine atom formed reacts with another methane molecule. The process continues until no more free radicals are produced. This may occur when two free radicals combine:



●Reactions that are a chain of consecutive conversions are called chain reactions. They proceed by the free-radical mechanism.

The Soviet scientist, Academician Semenov, made an important contribution to the development of the theory of chain reactions, for which he was awarded the Nobel Prize.

The Electron Structure of Halogen Derivatives. The highest electron density in a chloromethane molecule (the region where clouds overlap) is closer to the chlorine atom which is more electronegative. The chlorine atom thus becomes slightly negative, while the carbon atom becomes slightly positive:



The influence of the chlorine atom extends further into the molecule. In order to compensate for its positive charge, the carbon atom attracts the electron density of the C—H bonds. This partly accounts for the weaker bonds between the hydrogens and the carbon atom in the chloromethane molecule. Hydrogens in chloromethane can therefore be more readily replaced by chlorine than the first hydrogen atom in the methane molecule. But the atoms influence each other. The chlorine atom acts on the atoms of the methyl radical, but in turn it is influenced by the radical. The chlorine cannot for example be eliminated as the chloride ion $Cl^-$; nor is silver chloride precipitated when the halogen derivatives come into contact with silver nitrate.

Consider the electron structure of dichloromethane molecule $CH_2Cl_2$. Compare the positive charge on the carbon atom and the shift of the electron density along the C—H bonds with those in the chloromethane molecule $CH_3Cl$.

? 1. How can methane be distinguished experimentally from hydrogen?
△ 2. What volume of carbon dioxide (at STP) is formed after the combustion of 5 moles of methane?

3. What volume of hydrogen (at STP) is formed after the complete thermal decomposition of 2 moles of methane?
4. What volume of air (at STP) is needed to burn completely a mixture of 3 moles of methane and 20 litres of ethane?
5. Bromine acts on methane like chlorine. Write out the equations for the reactions of successive bromination of methane.
6. The electron pair in the chloromethane molecule is closer to the chlorine atom. The carbon atom becomes partly positive while the chlorine partly negative. Why are these charges only partial and not full?
7. Calculate how much heavier tetrachloromethane is with respect to air. Why is tetrachloromethane incombustible?
8. Write down equations for (a) reaction of decomposition of propane into the simple substances at high temperatures; (b) two or three of the reactions of the successive chlorination of propane. Explain how the reaction of decomposition of propane can be used to prove its molecular formula.
9. Give structural formulas for two homologues and two isomers of the substance with the formula $CH_3—CH_2—CH_2—CH_2—CH_3$.

## 2.3 Uses of Saturated Hydrocarbons and Their Manufacture

Uses of Alkanes. The high heat generated by the combustion of hydrocarbons accounts for their wide use as fuel, both in industry and in the home. Methane, which is the major component of natural gas, is especially widely used. Propane and butane (in the liquid state) are also currently used in areas remoted from the main lines through which natural gas is pumped from its deposits. Liquid hydrocarbons are used as fuel for internal combustion engines in automobiles, airplanes, etc.

Being an abundant gas, methane is also widely used as a raw material in the chemical industry.

The combustion and decomposition of methane are used for the manufacture of carbon black which in turn is necessary for the manufacture of rubber goods and printing ink. Methane is burned in special furnaces without enough air so that the combustion is incomplete. Part of the methane burns, while the other part is decomposed at high temperatures to give a fine carbon black.

Methane is also the source of hydrogen for the industrial synthesis of ammonia and some other organic compounds. The most popular method for preparing hydrogen from methane is by reacting it with steam. The reaction occurs at about 800 °C in the presence of a catalyst

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

The resultant mixture of gases is used for the synthesis of some products, but if pure hydrogen is required (e.g. for the manufacture of ammonia), the carbon monoxide is removed by catalytic oxidation with the steam

$$CO + H_2O \rightarrow CO_2 + H_2$$

Removal of carbon dioxide from the reaction products is quite easy. How would you remove the $CO_2$?

The chlorine derivatives of methane are obtained by chlorination. All these derivatives are valuable products.

Chloromethane (methyl chloride, $CH_3Cl$) is a gas. It is easily liquefied and absorbs a great deal of heat when subsequently evaporated. It is therefore used as a refrigerant.

Dichloromethane (methylene chloride) $CH_2Cl_2$, trichloromethane (chloroform) $CHCl_3$ and tetrachloromethane (carbon tetrachloride) $CCl_4$ are all used as solvents.

Tetrachloromethane is also used as fire extinguisher (especially in cases when water cannot be used for the purpose) because its heavy incombustible vapour separates the burning object from the oxygen of the air.

A great deal of hydrogen chloride is formed during the chlorination of methane, which dissolved in water gives hydrochloric acid.

Acetylene, which is widely used for the synthesis of many organic substances, has recently been prepared from methane.

Hydrocarbons with branched structure are obtained from the methane homologues by isomerization. They are used in the manufacture of synthetic rubbers and high-grade petrols. Higher hydrocarbons are used as raw materials for the manufacture of synthetic detergents.

Saturated hydrocarbons can be converted into unsaturated hydrocarbons, which are more active chemically, and are used for the synthesis of many organic substances.

Obtaining Alkanes. Saturated hydrocarbons are contained in large quantities in natural gas and petroleum. They are separated from these natural sources and used as fuel and raw materials in chemical industry.

The synthesis of methane is interesting from the theoretical point of view because it proves the possibility of preparing organic compounds from the simple substances. The reaction occurs by heating carbon with hydrogen in the presence of a powdered nickel catalyst

$$C + 2H_2 \rightarrow CH_4$$

Comparing this reaction with the thermal decomposition of methane (page 29), you see that the reaction is reversible. Adding the heat coefficient of the reaction we can write the following

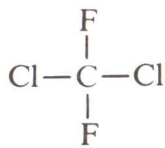
$$C + 2H_2 \rightleftarrows CH_4 + 75\ kJ$$

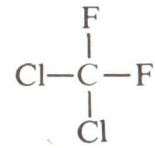
This equation suggests how the equilibrium of the reaction can be shifted to obtain methane, and conversely, how to carry out the reaction to decompose it. Since the synthesis of methane is an exothermic reaction, strong heating will not increase the yield of the product since the equilibrium will shift towards the formation of the carbon and hydrogen. However if the reactants are not heated enough the rate of methane formation will be low. The optimum temperature for the synthesis of methane is about 500 °C, and for its decomposition, over 1000 °C.

Pressure also affects the equilibrium of the reaction. The reaction proceeds to the right with a decrease in volumes. Higher pressure will therefore promote the formation of methane, while lower pressures will facilitate methane decomposition.

1. The reaction of methane with steam is reversible. Make the corresponding transformations in the equation given on page 33 and explain in which direction the chemical equilibrium will shift if the pressure is increased.
2. 2-Methylbutane can be obtained from *n*-pentane and is used for the synthesis of isoprene. Write out the corresponding reaction equation. What type of reaction is this?
3. Dichlorodifluoromethane (Freon 12) is used as a cooling agent in domestic refrigerators. This is an easily liquefiable gas. Draw the structural and electron formulas of dichlorodifluoromethane.

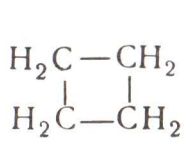
4. Construct models of (a) chloroethane, and (b) dichlorodifluoromethane. Use different colour plasticines for different atoms. Decide (by modelling) if one or two substances are described by the following formulas



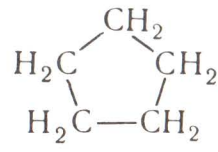


## 2.4 Cycloparaffins

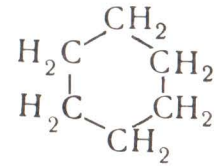
We have discussed saturated hydrocarbons with open chains of atoms. These are the paraffins or alkanes. But there are hydrocarbons with closed, or cyclic, structures. These are called the cycloparaffins:



Cyclobutane

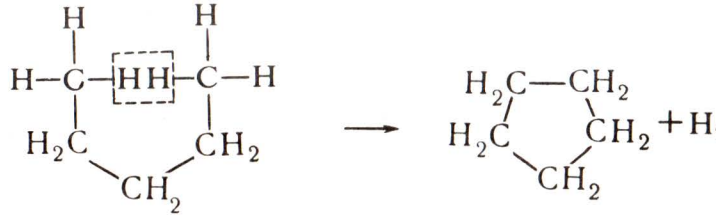


Cyclopentane

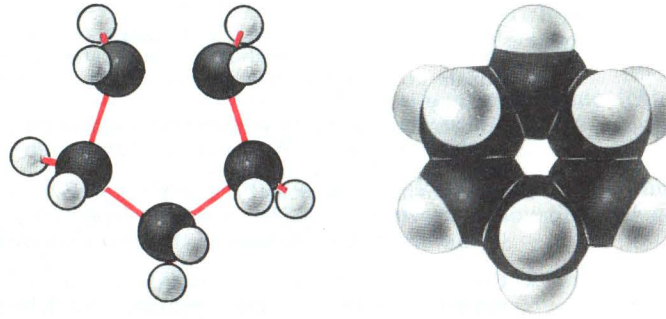


Cyclohexane

The cycloparaffins differ in composition from the corresponding paraffins in that they contain two hydrogen atoms less. The chain is closed into a ring at the point where the hydrogen atoms are eliminated. This can be shown schematically as follows



The general formula of the cycloparaffins is therefore $C_nH_{2n}$.

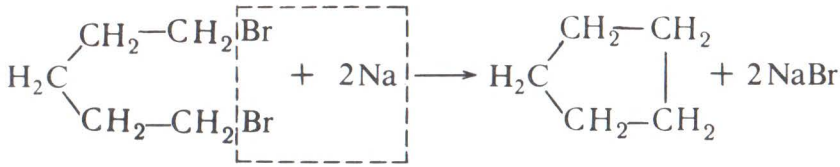


*a* *b*

Fig. 11. Models of cycloparaffin molecules:

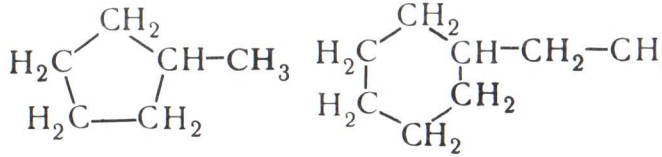
*a* – geometric model of cyclopentane; *b* – a scale model of cyclohexane (some hydrogen atoms are not seen)

In practice, cyclic hydrocarbons are synthesized in a different way, viz. through the dihalogen derivatives of hydrocarbons (heating in the presence of metal sodium):



To explain the conversion of pentane into cyclopentane, first remember that alkane molecules can assume different shapes because the carbon atoms rotate around their bonds. We have already mentioned that the terminal atoms may approach each other to a close distance, and hence the molecule can form a ring (Fig. 11).

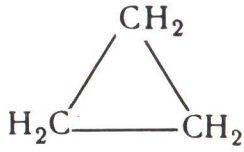
Cycloparaffin molecules often have lateral chains, e.g.



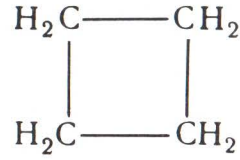
Methylcyclopentane Ethylcyclopentane

Cycloparaffins of these structures have much in common with the paraffins: their activity is low, they are combustible and their hydrogen atoms can be replaced by the halogens.

During the formation of the cycloparaffins with three or four carbon atoms, the valency bonds of the carbon atoms in the molecules deviate significantly from their initial orientation (i.e. from the angle of 109°28′) in the direction of the vertex. Stress develops in the cycles and they become less stable than the 5- or 6-membered cycloparaffins



Cyclopropane



Cyclobutane

Five- and six-membered cycloparaffins were first discovered by Markownikoff, a professor at the Moscow University. He discovered them in petroleum and hence called them naphthenes (from Greek *naphtha*, rock oil). They are the major component of many petroleums and important petroleum products.

1. Is cyclohexane (a) an isomer or (b) a homologue of *n*-hexane? Explain your answer.
2. Explain why cycloparaffins with three and four carbon atoms (in which the bond angle is less than 109°28′) are less stable?
3. Write down the reaction equations for (a) complete combustion of cyclopentane and (b) preparing of chlorocyclohexane from cyclohexane. Draw the electron formula of chlorocyclohexane.

4. Using plasticine, construct the models of (a) cyclopentane and (b) methylcyclopentane.
5. Using balls and rods, construct a model of 1,5-dibromopentane. Rotate its links to make sure that the molecule can under certain conditions form a ring.

# 3 Unsaturated Hydrocarbons

Unsaturated hydrocarbons are a large group of very important compounds. Let us get acquainted with their properties.

## 3.1 Structure of Hydrocarbons of the Ethylene Series (the Alkenes)

Like methane, which begins a series of saturated hydrocarbons, ethylene is the simplest unsaturated hydrocarbon.

Ethylene and Its Structure. Ethylene is a colourless gas, somewhat lighter than air, and almost odourless. Its hydrocarbon nature can be proved by examining its combustion products (much like we proved the qualitative composition of methane).

Let us determine its molecular formula. The density of ethylene under normal conditions is 1.25 g/litre. The molar weight of the gas is therefore 1.25 g/litre × × 22.4 litre/mol = 28 g/mol. Hence the molecular weight of ethylene is 28.

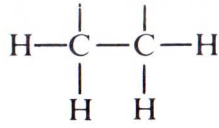
How many carbon and hydrogen atoms can be contained in such a molecule?

The molecule cannot contain one carbon atom because 16 hydrogen atoms would then have to be attached to it, but this is impossible. But the molecule may not contain more than two carbon atoms because their total weight is already 24. We have then to admit that the missing weight (28 – 24) is furnished by the hydrogen atoms (4 atoms). The molecular formula of ethylene is thus $C_2H_4$.

Now one can verify whether the gas is lighter or heavier than air.

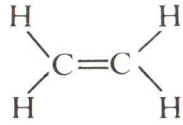
If we examine the formula of ethylene, we find a contradiction: the number of hydrogen atoms connected to the carbon atoms is smaller than the number of hydrogen atoms in the ethane molecule. How can then the carbon be tetravalent? In order to answer this question, let us consider the structure of the substance.

It has been established that the ethylene molecule is symmetrical, i.e. each carbon atom is connected to two hydrogens. If, as before, we use a dash to designate the bond between the atoms, the formula will look like this



It cannot express the structure of the ethylene molecule. The fourth valency units of the carbon atoms may not remain free, but they may join together to

form another bond between the carbon atoms:



Up till now we have only considered *single*, or ordinary, chemical bonds between atoms. We have found a new type of bond in the ethylene molecule: the *double bond*.

Since each valency unit of the carbon atom has unpaired electron in its outer layer, another shared electron pair is formed between the carbon atoms during the formation of the double bond:

Carbon thus remains tetravalent in the ethylene molecule and the octet rule holds for its atoms as well. Each valency dash in the structural formula describes a pair of electrons as before. But the following should be borne in mind. We mentioned earlier that the valency electrons form chemical bonds directed from the centre of the atom toward the vertices of the tetrahedron. However, in the case of ethylene, two bonds extend along one line, i. e. along the line connecting the centres of the carbon atoms. Let us consider the interaction of electrons during the formation of the double bond in more detail.

It has been established by physical methods that unlike the alkanes, the nuclei of the atoms in the ethylene molecule lie in the same plane and that the valency angles in the molecule are 120° and not 109°28′ (Fig. 12).

The known $sp^3$ hybridization theory, which accounts for the tetrahedral structure of the methane molecule, cannot explain the structure of the ethylene molecule. Only three of the four electron clouds of the excited carbon atom undergo hybridization, viz. one *s* and two *p* electron clouds. This is called $sp^2$ *hybridization*. The hybrid clouds have the same shape: they are asymmetrical dumb-bells elongated in one direction. Like in methane, they are as far apart as possible during the formation of chemical bonds. Why? The angle between the axes of electron clouds which are as far apart as possible is 120°.

But each carbon atom has one *p* electron more. Its cloud is not involved in hybridization, its shape remains unchanged (dumb-bell), and the electron density remains uniform on both sides of the nucleus. The axes of these electron clouds are perpendicular to the plane of the atomic nuclei because in this case they lie as far away as possible from the electron clouds involved in the formation of the chemical bonds. These dumb-bell electron clouds overlap partly above and below the nuclear plane to form another bond between the carbon atoms (Fig. 13*a*).

This lateral overlapping is however less significant than the overlapping of the clouds along the straight line connecting the centres of the atoms; this overlapping is remoted from them to a greater distance. The second bond in the ethylene molecule is therefore weaker than the first one. But as soon as it has been established, the atoms draw closer together. The bond length in the ethane

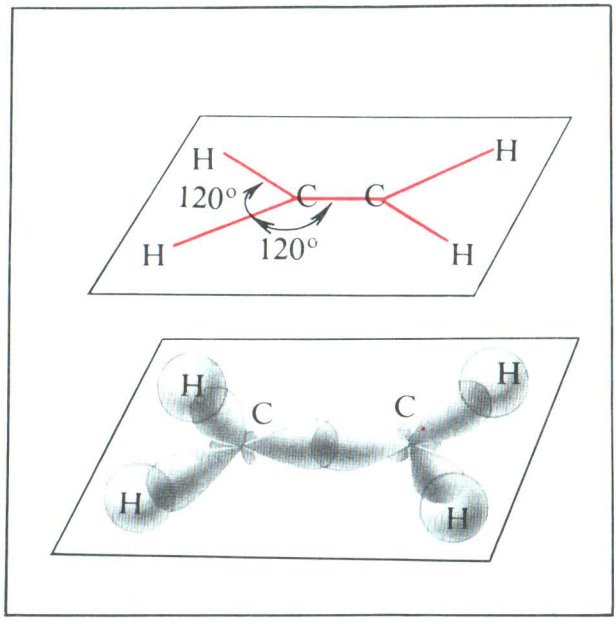



Fig. 12. Formation of σ bonds in an ethylene molecule

molecule is thus 0.154 nm while in the ethylene molecule it is 0.134 nm.

The first bond, which is stronger and is formed by overlapping electron clouds along the straight line connecting the centres of the atoms, is called a sigma (σ) bond, while the second weaker bond, which is formed by overlapping clouds above and below the plane of the atomic nuclei, is called pi (π) bond. The common carbon-hydrogen covalent bonds are σ bonds, hence saturated hydrocarbons only contain σ bonds.

The electrons of π bond (like those of σ bond) no longer belong to a definite atom but belong to, or are shared by both carbon atoms to form a common cloud, whose electron density is equally distributed above and below the plane of the σ bonds (Fig. 13*b*).

The structure of the ethylene molecule can be represented by rods and balls and also by a model in which the relative dimensions of the molecule are approximately correct (Fig. 14). In the former type, the double bond is given by two straight or curved rods, while in the model of the latter type the centres of the "carbon" balls are brought closer together.

The carbon atoms can only rotate in the molecule if they are connected by the σ bond; the π bond deprives them of this freedom of rotation. This can be understood if the electron structure of the molecules is considered in more detail (Fig. 12 and 13). Since the σ bond is directed along the straight line connecting the atoms, their rotation will not change the mode in which the clouds overlap; the atoms therefore remain chemically bonded. If the atoms are connected by a double bond, their rotation becomes possible only if the electron

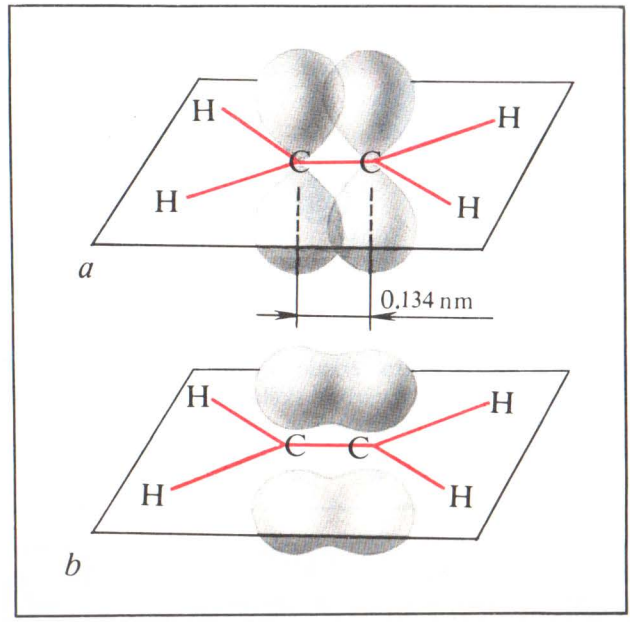



Fig. 13. Formation of π bond in an ethylene molecule:
*a* lateral overlapping of *p* electron clouds; *b* – distribution of the π bond cloud above and beneath the plane of the atomic nuclei

clouds of the π bond separate. But this would mean that the electron structure of the molecule would be changed.

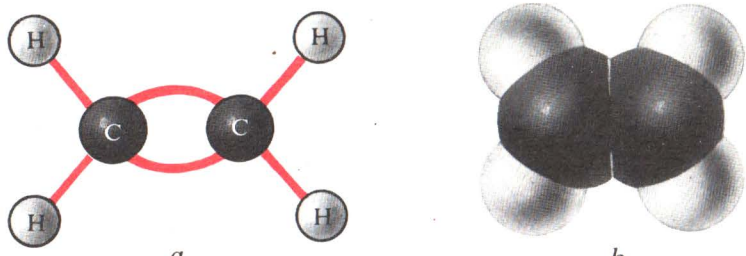
We shall learn later what are the consequences of the absence of the free rotation in double bonding.

Structure and Nomenclature of Ethylene Series Hydrocarbons. Ethylene is the first member of a homologous series of substances whose molecules contain double bonds between carbon atoms (see Table 3.1). The next homologues of ethylene are propylene $CH_2{=}CH{-}CH_3$ and butylene $CH_2{=}CH{-}CH_2{-}CH_3$. The names of hydrocarbons of the ethylene series are formed by changing the *-ane* ending of the corresponding saturated hydrocarbon for *-ene*.

The homologues in the series differ by the $CH_2$ grouping. Make sure that this condition is fulfilled in this series of substances.

The molecule of each of these unsaturated hydrocarbons has one double bond and therefore each has two hydrogens less than the corresponding saturated hydrocarbon. The composition of the ethylene series hydrocarbons is therefore expressed by the general formula $C_nH_{2n}$. What other hydrocarbons have the same general formula?

Unsaturated hydrocarbons may form radicals. For example, the univalent radical of ethylene has the structure $CH_2{=}CH{-}$ or $H{:}\,\dot{\underset{\cdot\cdot}{C}}{::}C{\cdot}$ and is called *vinyl*.




*a* *b*

Fig. 14. Models of an ethylene molecule:

*a* – geometric model; *b* – scale model

Isomerism is also a characteristic of unsaturated hydrocarbons. Like the saturated hydrocarbons, the carbon skeleton can be isomerized. The following are two isomers of the hydrocarbon with the formula $C_5H_{10}$:

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3 \qquad CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$$

However, isomerism also depends on the position of the double bond in the carbon chain. Substances with the formula $C_5H_{10}$ may therefore have the following structures

$$CH_3{-}CH{=}CH{-}CH_2{-}CH_3 \qquad CH_3{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$$

Two types of isomerism thus occur in the series of ethylene hydrocarbons: isomerism of the carbon skeleton and that of the position of the double bond. The former is called *chain* or *nuclear* isomerism, and the latter, *position* isomerism.

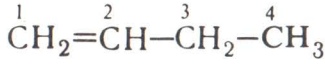
The individual names for the isomers of ethylene hydrocarbons are derived as follows. The longest chain of carbon atoms containing the double bond is first chosen. The carbon atoms are then numbered consecutively from the end of the

*Table 3.1*

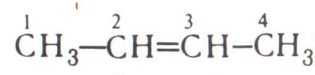
THE ETHYLENE SERIES (AS COMPARED WITH SATURATED HYDROCARBONS)

| Saturated hydrocarbon | Unsaturated hydrocarbon |
|---|---|
| Methane $CH_4$ | – |
| Ethane $C_2H_6$ | Ethylene (ethene) $C_2H_4$ |
| Propane $C_3H_8$ | Propylene (propene) $C_3H_6$ |
| Butane $C_4H_{10}$ | Butylene (butene) $C_4H_8$ |
| Pentane $C_5H_{12}$ | Pentene $C_5H_{10}$ |
| Hexane $C_6H_{14}$ | Hexene $C_6H_{12}$ |
| etc. | |

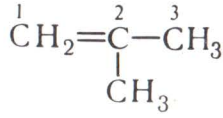
chain nearest to the double bond. The position of the double bond is indicated at the end of the name by the number of the carbon atom at which the double bond originates. The position of the side chain is indicated by the figure that comes before the name of a substance:



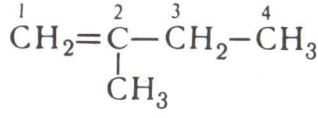
Butene-1



Butene-2



2-Methylpropene
(isobutylene)



2-Methylbutene-1

Name the hydrocarbons whose structural formulas are given above without names.

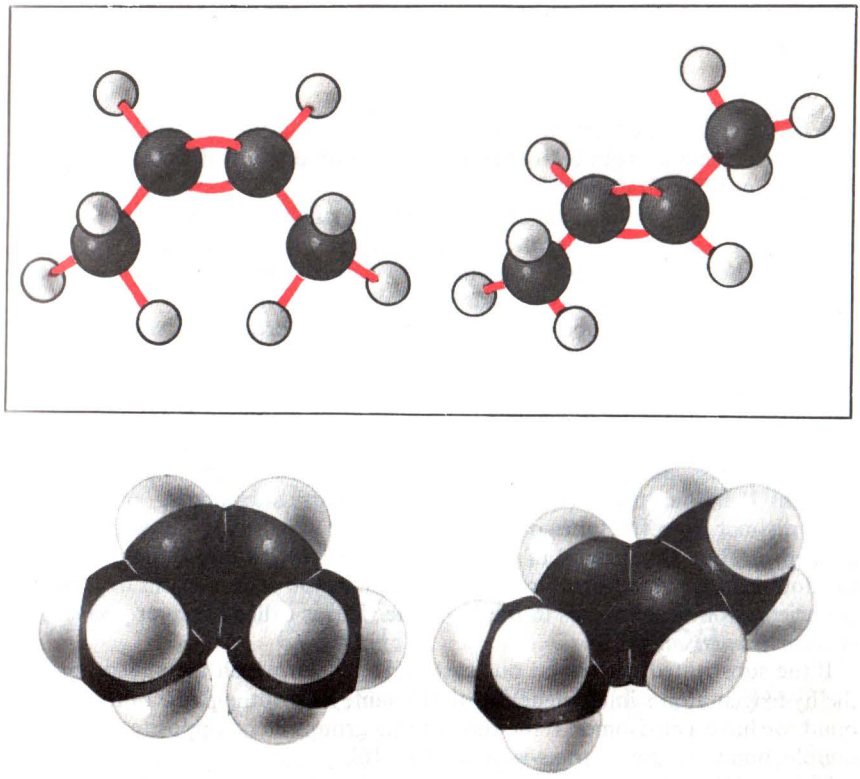


Fig. 15. Geometric and scale models of spatial isomers of butene

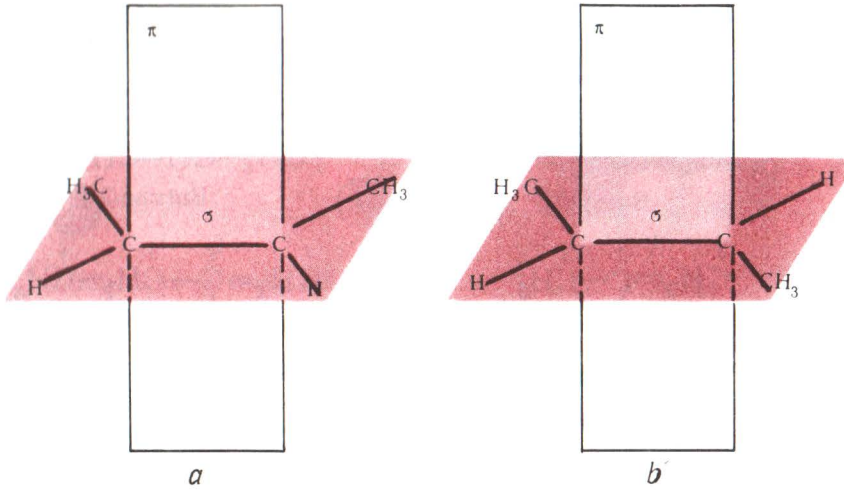



Fig. 16. *Cis-trans* isomerism of butene-2:

*a* – *cis*-isomer; *b* – *trans*-isomer

When we discussed ethylene we noted that the atoms connected by the double bond cannot rotate. This gives rise to another type of isomerism which we have not yet discussed.

The molecule of butane can be represented in different ways. It can be either a zigzag or a curved molecule. These different models represent the same substance because the carbon atoms in saturated hydrocarbons can freely rotate, and one form easily transforms into another.

Consider now the structure of an unsaturated hydrocarbon with the same number of carbon atoms.

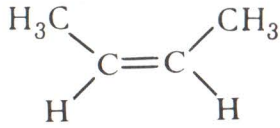
The model of butene-2 can also be represented in two forms (Fig. 15). But two carbon atoms in its molecule are connected by a double bond and cannot rotate. (Remember why.) The configuration of this molecule cannot therefore be changed unless additional energy is applied. If we obtain molecules with different configurations, they will be different substances, or isomers.

As distinct from the types of isomerism which we already know and which depend on the arrangement of the atoms in the molecules and the position of the double bond (structural isomerism), the new type of isomerism depends on the orientation of the atoms in the molecule. This is called *space* or *geometrical* (*stereo*) *isomerism.*

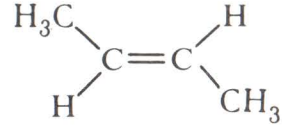
If the substituted groups (in our case $CH_3$ groups which are substituted for the hydrogen atoms in ethylene) lie on the same side of the plane of the double bond, we have a *cis*-isomer. If the substituting groups lie on opposite sides of the double bond we get a *trans*-isomer (Fig. 16).

This is called *cis-trans* isomerism (from Latin *cis* meaning on this side, and *trans* meaning across or over). This type of isomerism is represented by the

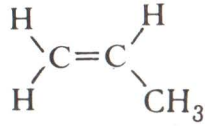
following structural formulas



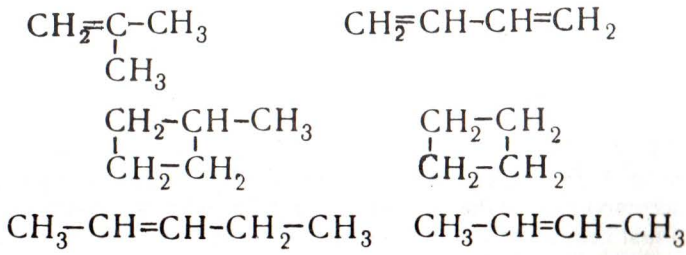
*cis*-isomer
(m.p.-138.9°C
b.p. 3.7°C)



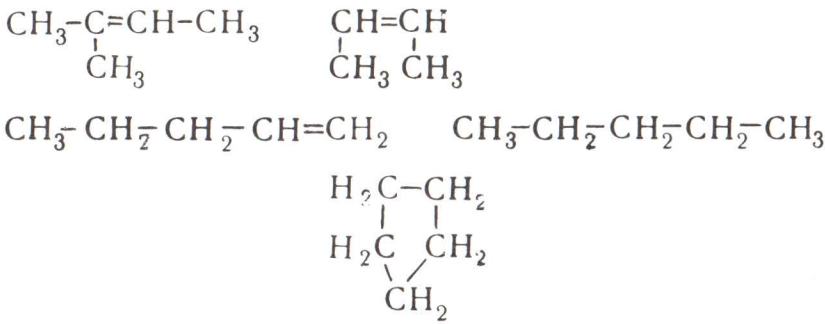
*trans*-isomer
(m.p.-105.5°C
b.p. 0.9°C)

It is easy to see that this type of isomerism (geometrical isomerism) occurs whenever two dissimilar atoms or atomic groups are connected to carbon atoms on either side of a double bond. If one of the carbon atoms is connected not with dissimilar but identical atoms or groups of atoms, *cis-trans* isomerism will not occur. Whichever side of the double bond the methyl group lies on, the compound  will remain the same.

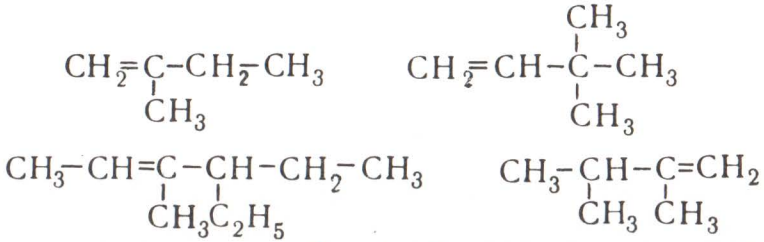
1. Calculate the density of ethylene relative to (a) hydrogen and (b) air.
2. What is the difference between the σ and π bonds in the ethylene molecule?
3. Explain why carbon atoms connected by the double bond cannot rotate freely?
4. Explain why the bond length between the carbon atoms in the ethylene molecule is shorter than that in the ethane molecule.
5. Determine the molecular formula of a gaseous hydrocarbon if 5.6 litres (at STP) of it burn to give 16.8 litres of carbon dioxide and 13.5 g of water.
6. Determine the molecular formula of a hydrocarbon in which the weight fraction of carbon is 85.7 per cent, and the density relative to hydrogen is 28.
7. Draw the structural formulas of the isomers of a hydrocarbon whose molecular weight is 56.
8. A hydrocarbon has the formula $C_6H_{12}$. Can it be concluded from the formula that this hydrocarbon belongs to the homologous series of ethylene?
9. Indicate which of the following substances are isomers:



10. Consider the formulas below and decide which of the indicated compounds are (a) isomers and (b) homologues of pentene-2 ($CH_3—CH=CH—CH_2—CH_3$):



11. Name the following hydrocarbons



12. Draw the structural formulas of the following hydrocarbons: (a) 3-ethylheptene-2, (b) 3,3-dimethylpentene-1, (c) 3-methyl-4-ethylhexene-2.
13. Which of the following compounds have *cis-trans* isomerism: (a) butene-1; (b) pentene-2; (c) 2-methylbutene-2; (d) 2-methylpropene? Write down the formulas for the isomers.

■ 14. Construct models to prove whether *cis-trans* isomerism is possible in (a) isobutylene of (b) 1,2-dichloroethene CHCl=CHCl.

## 3.2 Chemical Properties of Ethylene Series Hydrocarbons. Mechanism of Addition Reactions

Chemical Properties. Saturated and unsaturated hydrocarbons consist of the same elements, i. e. carbon and hydrogen, and for this reason they have one common property: they are flammable. Ethylene, for example, when lighted, burns in air to give water and carbon dioxide

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O + Q$$

In contrast to methane, it burns with a luminescent flame which is mainly due to a high carbon content. The carbon liberated during the thermal decomposition of the ethylene molecules does not burn at once and particles of it first heat up to cause luminescence of the flame, and then burn in the outer zone of the flame.

While similar in the element composition, ethylene and its homologues differ from the alkanes in structure: they contain a double bond. Do the chemical properties of these compounds depend on this fact?

Let us see what action the agents we used for testing methane and its homologues have on alkenes.

If we pass ethylene into a solution of potassium permanganate the violet colour soon vanishes to indicate that $KMnO_4$ oxidizes the ethylene. Saturated hydrocarbons, as you may remember, are not oxidized in this way. Other hydrocarbons with double bonds are also readily oxidized.

When ethylene is oxidized by potassium permanganate, a dihydric alcohol ethylene glycol is produced. If we designate conventionally the oxidant as an oxygen atom, the equation of reaction will be as follows

$$CH_2{=}CH_2 + O + H_2O \longrightarrow \underset{\displaystyle OH}{\overset{\displaystyle CH_2}{|}} - \underset{\displaystyle OH}{\overset{\displaystyle CH_2}{|}}$$

If we pass ethylene and methane through bromine water (an aqueous solution of bromine), the brownish red colour of bromine will vanish when ethylene is passed. Methane has no effect on bromine water. This means that in this particular case ethylene is more reactive than the saturated hydrocarbons. The reaction of ethylene with bromine gives a colourless liquid, dibromoethane $C_2H_4Br_2$; i.e. the bromine molecules become attached to the ethylene molecules

$$CH_2{=}CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\overset{\displaystyle CH_2}{|}} - \underset{\displaystyle Br}{\overset{\displaystyle CH_2}{|}}$$

The bromine atoms are attached at the double bond which is thus converted into a single bond. Some other alkenes also readily attach bromine:

$$CH_2{=}CH{-}CH_3 + Br_2 \longrightarrow \underset{\displaystyle Br}{\overset{\displaystyle CH_2}{|}} - \underset{\displaystyle Br}{\overset{\displaystyle CH}{|}} - CH_3$$

1,2-Dibromopropane

Potassium permanganate and bromine water are reagents for alkenes: the change in colour indicates the presence of alkenes.

In the presence of a catalyst (nickel or platinum), hydrogen can be added to alkenes at the double bond:

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$$

$$CH_2{=}CH{-}CH_3 + H_2 \rightarrow CH_3{-}CH_2{-}CH_3$$

In this reaction, *unsaturated* hydrocarbons thus react with the hydrogen to form *saturated* hydrocarbons.

Reactions by which hydrogen is attached to a substance are called *hydrogenation* reactions. In the example above, ethane and propane are prepared by hydrogenation of ethylene and propylene.

During hydrogenation, the carbon atoms at the double bond go from the $sp^2$ hybridization to the $sp^3$ hybrid state and the spatial structure of the molecule is thus changed. The planar molecule of ethylene is hydrogenated into the three-dimensional molecule of ethane. Consider the change in the molecular structure that occurs during hydrogenation of propylene.

Unsaturated hydrocarbons can enter addition reactions not only with simple but also composite substances. Ethylene, for example, readily reacts with hydrogen bromine:

$$CH_2{=}CH_2 + HBr \rightarrow \underset{\text{Bromoethane}}{CH_3{-}CH_2Br}$$

The halogen derivatives of saturated hydrocarbons can thus be prepared from the alkenes.

Molecules of ethylene hydrocarbons can also combine with one another to form long chains. For example, polyethylene, a well-known plastic, is prepared from ethylene at high temperatures and pressures. Hundreds and thousands of ethylene molecules combine into long chains as indicated below

$$CH_2{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + \ldots \rightarrow$$
$$\rightarrow -CH_2{-}CH_2- + -CH_2{-}CH_2- + -CH_2{-}CH_2- \ldots \rightarrow$$
$$\rightarrow -CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2- \ldots$$

A high-molecular substance is thus formed. It is known as *polymer*. ● The union of identical molecules into larger molecules is called polymerization. The polymerization of ethylene can be described more briefly as

$$n CH_2{=}CH_2 \rightarrow (-CH_2{-}CH_2-)_n$$

Propylene can be polymerized in a similar way to give polypropylene, which has similar properties to polyethylene:

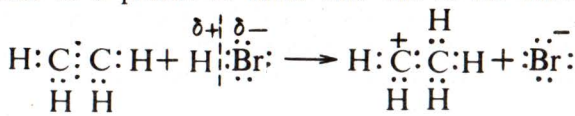
$$n\,CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{CH}} \longrightarrow \left(-CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}-\right)_n$$

It can be seen from these examples, that the double bond is not merely the sum of two single bonds. It is a qualitatively different bond, in which one bond is weaker and this accounts for the reactivity of the substance.

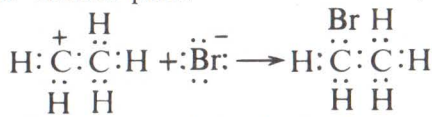
Mechanism of the Addition Reaction. Earlier we discussed the substitution reaction, which is more characteristic of saturated hydrocarbons. Let us now consider the mechanism of the addition reaction, which is more characteristic of unsaturated hydrocarbons.

As distinct from the substitution reaction, which occurs through formation of free radicals, the addition reaction has an *ionic mechanism*.

Consider first the reaction of ethylene with hydrogen bromide. The covalent bond in the hydrogen bromide molecule is polar. The electron density of the bond is displaced in the direction of the more electronegative element, thus the hydrogen atom is partly positively charged, while the bromine atom is partly negatively charged. As the positively charged hydrogen atom approaches an ethylene molecule, it interacts with the $\pi$ bond electrons (which are somewhat "outside" the molecule). It attracts them and separates from the hydrogen bromide molecule as a proton to unite with one of the carbon atoms:

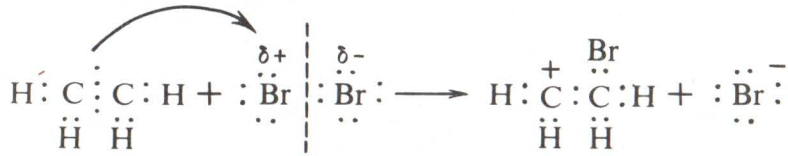


The break down of the H—Br bond occurs by the ionic mechanism. The second carbon atom, which has lost its electrons, becomes positively charged (due to the charge on the nucleus). This positively charged atom attracts the negatively charged bromide ion and a covalent bond is formed between them using one of its electron pairs:

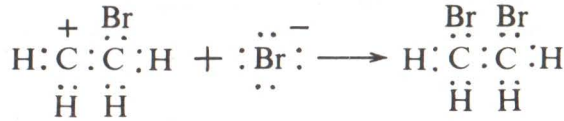


The same mechanism is used for the combination of the halogens, e.g. bromine, with ethylene (see equation above).

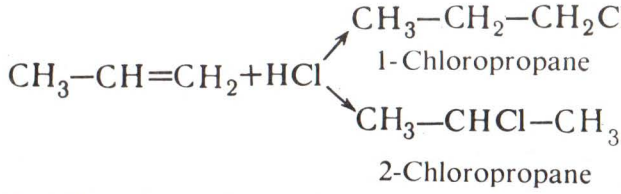
The bromine molecule approaches the ethylene molecule and becomes polarized because the electrons of the bromine's chemical bond are displaced from one atom to the other by the action of the electron cloud of the π bond. Partly positive bromine atom attracts the π electrons of the ethylene molecule and uses them to bond to one of the carbon atoms:



The negatively charged bromide ion then uses an electron pair and bonds to the other positively charged carbon atom. 1,2-Dibromoethane is thus formed:



The addition of complex substances to ethylene homologues has a special feature. It can be suggested that the reaction, e.g. of hydrogen chloride and propylene, will proceed in one of the following directions or a mixture of two substances with different position of the halogen atom may be obtained:



1-Chloropropane

2-Chloropropane

Markownikoff established that the reaction occurs mainly in the second direction, i.e. hydrogen unites with the carbon atom at the double bond that is bonded to the greater number of hydrogen atoms, while the halogen is attached to the carbon atom which is bonded to the smaller number of hydrogen atoms. This is known in chemistry as *Markownikoff's rule*. How can this regularity be explained?

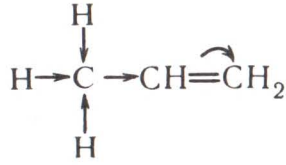
Propylene differs from ethylene by the presence of the $CH_3$ radical. The effect

Vladimir Vasilyevich
MARKOWNIKOFF (1838–1904)

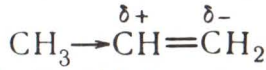
Vladimir Markownikoff was a professor at Moscow University and a pupil of Butlerov. He synthesized several compounds predicted by the theory of chemical structure. He developed Butlerov's ideas about the mutual effects of atoms inside molecules and established some regularities in this field. A great deal of his work was devoted to the study of the natural wealth of Russia, especially the petroleum deposits. Markownikoff discovered a new class of hydrocarbons, the naphthenes (cycloparaffins) in the petroleum extracted in the Caucasus and investigated them thoroughly. He also studied the composition of the water of salt lakes and mineral sources of Russia.

of this radical on the double bond probably explains why the addition occurs in a definite direction. But what actually is the effect?

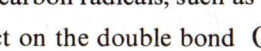
The C—H bonds in the methyl radical are only slightly polar because of the different electronegativities of the elements. The carbon atom attracts the electron density of the bonds with the hydrogen atoms to become partly negative. The electron density of the bond between the radical and the neighbouring carbon atom is displaced towards the carbon atom to displace the mobile cloud of the $\pi$ bond towards the terminal carbon atom. All these shifts can be shown in the structural formula as



The double bond is thus no longer symmetric and becomes polarized:



The positively charged hydrogen ion of the hydrogen chloride molecule will of course unite with the $CH_2$ link (the one containing the greater number of hydrogen atoms) which is partly negative, whereas the negatively charged chloride ion will attach to the CH link. The mechanism of the reaction is thus ionic as well.

Other hydrocarbon radicals, such as the ethyl in butene-1 will have the same polarizing effect on the double bond  . A hydrogen halide will be attached according to the Markownikoff's rule as well.

1. How does the spatial structure of the ethylene molecule change when hydrogen bromide is added to it? Explain your answer.
2. How can methane be separated from ethylene?
3. After ethylene was passed through bromine water, the liquid's weight increased by 14 g. What volume of ethylene (at STP) was absorbed? What is the weight of the resultant dibromoethane?
4. Prove experimentally that the gas which is used as fuel in a laboratory, in industry, and in the home, contains an unsaturated hydrocarbon.
5. A mixture of methane and propylene burns with a luminescent flame. If the gas mixture is passed through bromine water, the flame's luminescence is decreased. Explain.
6. The molecular weight of a product of a reaction between an unsaturated hydrocarbon and chlorine is 113. Determine the formula of the hydrocarbon.
7. What volume of hydrogen can combine with (a) 100 ml of propene, (b) 3.5 g of pentene?
8. Compare the properties of propylene and propane. Which of them are different and which are common? Illustrate your answer by reaction equations.
9. What is the difference between the mechanisms of the substitution reactions of saturated hydrocarbons and the addition reactions of unsaturated hydrocarbons? Illustrate your answer by examples.
10. Write down the equation for the reaction between butylene (butene-1) and hydrogen bromide. Name the resultant product. Explain the mechanism of the reaction.
11. Hydrogen bromide reacts with trifluoropropene $CF_3—CH=CH_2$ contrary to the Markownikoff rule. Explain why.

## 3.3 Uses of the Ethylene Series Hydrocarbons and Their Manufacture

Uses of the Ethylene Hydrocarbons. The high chemical activity of the ethylene hydrocarbons accounts for their wide use as raw materials for the manufacture of many organic substances. They are not therefore used as fuels.

We shall often discuss the synthesis of organic products from unsaturated hydrocarbons. Ethylene is especially widely used for the purpose.

The reaction of ethylene and chlorine gives 1,2-dichloroethane:

$$CH_2=CH_2 + Cl_2 \rightarrow CH_2Cl—CH_2Cl$$

Dichloroethane is a volatile liquid that burns with difficulty. It is a good solvent for many organic substances and is therefore used for dissolving resins, for dry cleaning textiles, etc. It is a good pesticide and is used in agriculture to control phylloxera of grapes and to disinfect granaries.

Chloroethane (ethyl chloride) is obtained by adding hydrogen chloride to ethylene:

$$CH_2=CH_2 + HCl \rightarrow CH_3—CH_2Cl$$

It is a gas at ordinary temperatures, but is easily converted into a colourless liquid (see Appendix, Fig. III). If a small quantity of ethyl chloride is placed on the hand, the liquid will soon evaporate cooling noticeably the skin. For this property it is used as an anaesthetic in minor surgical operations.

Hydration of ethylene is the major reaction in the manufacture of ethyl alcohol, which is used in large amounts in the manufacture of synthetic rubber

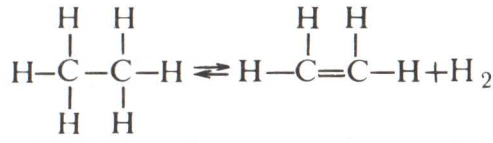
$$C_2H_4 + H_2O \rightarrow \underset{\text{ethyl alcohol}}{C_2H_6O}$$

Propylene and ethylene can be polymerized into polypropylene and polyethylene, the materials widely used in everyday life.

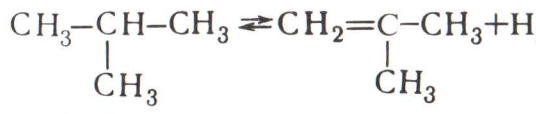
Ethylene has a specific property to accelerate the ripening of fruits and vegetables (pears, melons, lemons, tomatoes, etc.). Unripe fruits and vegetables can be shipped to a storehouse, where a small amount of ethylene is added to the air. This reduces spoilage during transportation.

Manufacture of Ethylene Hydrocarbons. Since the ethylene series hydrocarbons are chemically active, they do not occur in nature. It is difficult to imagine what might happen if these hydrocarbons were contained in, e.g. natural gas or petroleum, which occur in underground deposits at high pressures.

In industry these hydrocarbons are obtained by processing petroleum products at high temperatures, by *dehydrogenation* of saturated hydrocarbons, i.e. by eliminating hydrogen from them:



Ethane Ethylene



Isobutane Isobutylene

Earlier we discussed the opposite process: hydrogenation of hydrocarbons. Therefore, it follows that this reaction is reversible.

Various methods are used for preparing unsaturated hydrocarbons in the laboratory. Ethylene, for example, is prepared from ethyl alcohol $C_2H_6O$ by eliminating water from it (by heating it with sulphuric acid), i.e. by carrying out the process which is reverse to that by which ethyl alcohol is manufactured in industry (Fig. 17)

$$C_2H_6O \rightarrow C_2H_4 + H_2O$$

? 1. Write equations for the hydrogenation of propylene and the dehydrogenation of propane. Express these processes in a single equation. Remember that the hydrogenation is an exothermic reaction. Explain in which direction the equilibrium will shift if (a) temperature is raised, or (b) pressure is increased.

△ 2. Which two methods for preparing ethyl chloride do you know? Give the corresponding equations.

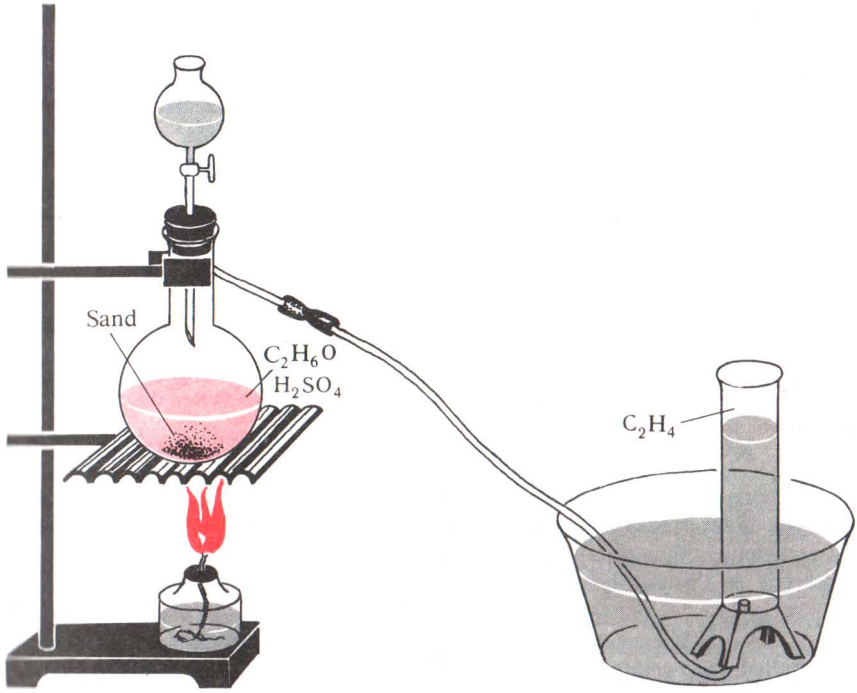



Fig. 17. Preparing ethylene

3. What quantity, in grams, of dichloroethane can be prepared from a mixture of 1 mole of ethylene and 11.2 litres of chlorine (at STP)?
4. Tetrafluoroethylene $CF_2{=}CF_2$ is used for the manufacture of a polymer which is very stable chemically. Neither acids, nor ordinary oxidants act on it at high temperatures. Write a reaction scheme for the polymerization of tetrafluoroethylene (follow the pattern given for the polymerization of ethylene).
5. Name some of the halogen derivatives of hydrocarbons that are used as (a) solvents, (b) refrigerants, and (c) fire extinguishers.

■ 6. Construct a model to show the changes in the spatial structure of the propylene molecule that occur when it is hydrogenated.

## 3.4 High-Molecular Compounds

When we studied the alkenes we learnt about their ability to polymerize into high-molecular compounds. High-molecular polymers consist of gigantic flexible molecules which consist of repeated structural units (groups of atoms). Synthetic fibres, rubbers, and many other everyday materials are high-molecular compounds.

Synthesis of Polymers and Their Structure. There are two main methods by which high-molecular substances are synthesized: addition polymerization and

condensation polymerization.* Let us consider the polymerization of ethylene in more detail. It proceeds by the free-radical mechanism. The formation of free radicals is promoted by the addition of a special initiator. The initiator for the polymerization of ethylene under a high pressure (up to 150 MPa) is oxygen. Oxygen reacts with ethylene to give unstable compounds, which readily decompose into free radicals (R·). When the radical collides with a molecule of ethylene, the free electron interacts with the π bond to form a pair with one of its electrons thus establishing a covalent bond between the radical and the ethylene molecule. The second electron of the π bond remains free and the entire particle turns into a free radical

$$R^{\bullet} + CH_2{:}\,CH_2 \longrightarrow R{:}CH_2{:}CH_2^{\bullet}$$

This radical then acts similarly on another ethylene molecule, which is attached to give a new radical:

$$R{:}CH_2{:}CH_2^{\bullet} + CH_2{:}\,CH_2 \longrightarrow R{:}CH_2{:}CH_2{:}CH_2{:}CH_2^{\bullet}$$

This consecutive attachment of molecules in the chain reaction continues until the chain breaks (e.g. when the growing radicals unite with one another). Polyethylene is thus obtained. Its molecular weight may range from dozens to hundreds of thousands: $(-CH_2-CH_2-)_n$.

● The low-molecular substance from which polymer is synthesized is called a monomer. Ethylene and propylene are monomers. Polymer molecules are also called *macromolecules* (from Greek *makros*, long).

The groups of atoms that are repeated in the macromolecule are called its *structural units* (or repeated units). The structural units of polyethylene and polypropylene are

$$-CH_2-CH_2- \quad \text{and} \quad -CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

● The number *n* shows the number of molecules of the monomer that are united in a macromolecule, and is called the degree of polymerization (DP).

By their geometrical configuration, the discussed polymers are linear because their structural units combine consecutively into chains. We shall later discuss polymers with branched, and three-dimensional structures. Network or cross-linked structures have additional chemical bonds between the linear chains (Fig. 18).

The length of a linear molecule is thousands of times greater than its cross section. If we imagine a macromolecule as a thread 1 mm in diameter, it would be several metres long. It should, however, be remembered that linear-chain molecules are not straight. We already know that carbon atoms can form zigzags; the molecules are thus usually bent in various directions, and sometimes even coiled.

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* Polycondensation (condensation polymerization) will be discussed below (p. 120).

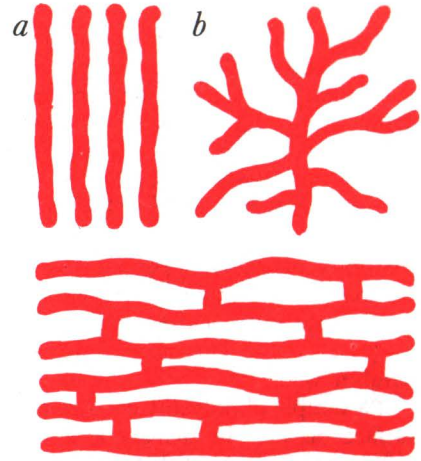



Fig. 18. Geometric form of macromolecules of polymers:

*a* – linear; *b* – branched; *c* – three-dimensional

The concept of the *molecular weight* is slightly modified when one speaks of polymers. The number of monomers polymerized into macromolecules is not strictly defined: some chains contain fewer and others greater number of repeated units. The number depends on the moment when the growth of the chain is terminated. Macromolecules of various lengths are thus formed and their molecular weight differs accordingly. If a molecular weight is indicated for a polymer, it means an average molecular weight, from which the actual weight of the separate molecules deviates substantially in both directions. If the molecular weight of a polymer is, say 28,000, it may contain molecules with molecular weights of 26,000, 28,000, or 30,000.

Properties of Polymers. Consider the properties that depend on the structure of polymers.

Low-molecular substances are usually characterized by definite melting and boiling points, and other parameters.

If a polymer with a linear structure is heated, it will first soften and only later, as the temperature increases, it will gradually melt into a viscous liquid. If the temperature increases further, the polymer will decompose without evaporating. It is impossible to distil polymers. Many polymers are poorly soluble, and even then the solutions are very viscous.

An important property of polymers is their high mechanical strength, which in combination with other valuable properties (light weight, chemical stability, etc.) accounts for their wide use.

How can these properties be explained? In order to melt, dissolve, or evaporate a substance, the force of mutual attraction between the molecules should be overcome by heating or by the action of a solvent. The interaction between molecules in a high-molecular substance is much stronger than that in a low-molecular substance because the molecules are attracted to one another by a huge number of links. When we heat a polymer and it begins to soften, this means that the intermolecular forces between the macromolecules have weakened and they can move relative to one another due to thermal motion. The larger macromolecules interact more strongly and therefore require more

heat to become mobile. This explains why a high-molecular substance does not melt at strictly definite temperature.

Distillation of a substance becomes possible when it is heated to higher temperatures. The gigantic molecules of polymers might probably become volatile at very high temperatures, but they cannot stand such a heating, because the chemical bonds between their atoms break, and the substance decomposes before it is distilled. The small molecules of solvents can barely pull the polymer molecules apart which accounts for the comparatively poor solubility of many polymers.

Finally, the mechanical strength of high-molecular substances also depends on the presence of the strong intermolecular interactions.

Polyethylene. This is a white greasy to touch solid material resembling paraffin wax.

If a sample of polyethylene is placed in a flask with water, it will float on the surface because its density is about 0.92 g/cm$^3$.

Try to break a polyethylene object or to tear a polyethylene film and you will see how tough the material is. It is easy to show that polyethylene does not conduct electricity.

When heated, polyethylene softens and easily changes its shape. When cooled, it sets in the new shape. If heated again, the polyethylene will soften again, etc.

The ability of substances to become soft and moldable when subjected to heat is called *thermoplasticity*. Thermoplastic polymers can thus be shaped into a variety of articles and, if necessary, can undergo secondary heat treatment. Thermoplasticity is a property of many polymers.

The chemical properties of polyethylene can be guessed to a certain degree, because this polymer not only looks like the paraffin wax, but has a structure similar to saturated hydrocarbons.

When ignited, polyethylene burns with a blue weakly luminescent flame. What are the products of this reaction?

If we place polyethylene in sulphuric acid, an alkali, bromine water, or potassium permanganate solution, no chemical changes will be noticed at room temperature. This is characteristic of saturated hydrocarbons. Acids can only destroy polyethylene at high temperatures.

Many of the uses of polyethylene are well known. It is widely used as an insulator in electrical engineering. Being impermeable to water and gas, polyethylene is used as a packaging material for food, many other articles, and even for machines. Polyethylene is used in agriculture to protect fruit trees and seedlings from frost, etc.

The chemical stability of polyethylene accounts for its use in the manufacture of chemical apparatuses, containers for storage and for shipping corrosive liquids, etc. This property is also valuable in the manufacture of water-supply pipes (Fig. 19). Flasks, cups, bottles, bags and many other objects that we use in everyday life are also manufactured from polyethylene.

When using these articles one should remember that polyethylene softens at 110–130 °C and loses its initial shape. The polymer should not therefore be exposed to high temperatures.

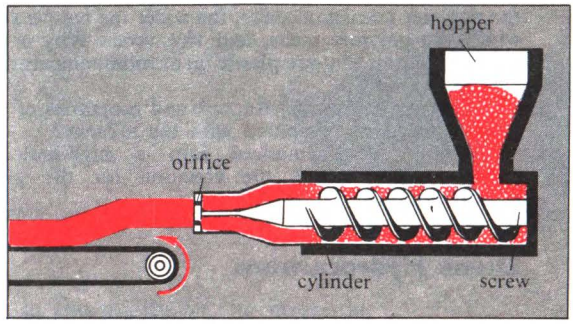



Fig. 19. Manufacture of polyethylene tubes by extrusion. Polyethylene is softened in an electrically heated cylinder and extruded by the screw through an annular orifice. When cooled the tube retains its shape

Polyethylene was once obtained in industry only by the high-pressure process and at a temperature of 200 °C. But pressure vessels are more difficult to construct and high-pressure processes are more difficult to control. Furthermore, the structure of the resultant polymer is not strictly linear and is somewhat branched.

At the present time polyethylene is also prepared by a low-pressure techniques in the presence of catalysts. "Low-pressure" polyethylene has a higher molecular weight and is less branched. The intermolecular interaction in this polymer is stronger and its properties in some aspects are better than those of "high-pressure" polyethylene: it softens at higher temperatures and is mechanically stronger.

Polypropylene has many properties in common with polyethylene. This is also a solid substance oily to touch. Its colour is milk-white. Like polyethylene, it is thermoplastic and is chemically stable. As distinct from polyethylene, polypropylene softens at higher temperatures (160–170 °C) and is mechanically stronger. It is now widely used in the manufacture of high-strength insulation, cables, pipes, chemical apparatuses, and various other articles.

? △

1. What is common and what is the difference between the molecule of the monomer and the structural unit of the polymer it forms?
2. The structure of a well-known material, polyvinyl chloride is

$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\ldots$$

Identify the repeat unit of the polymer and determine the structural formula of the monomer.

3. Polyethylene with the molecular weight of about 500 is a viscous liquid. Calculate its degree of polymerization.
4. What is the difference between the concepts of molecular weights of low- and high-molecular substances?
5. Explain (a) the absence of volatility in high-molecular compounds, (b) viscosity of their solutions.
6. It has been established that the greater the difference in the weights of

the polymer macromolecules, the wider the temperature range within which the polymer melts, and vice versa. Why is this?

7. Name materials that are plastic (a) at room temperature, and (b) when heated.
8. What is common to the structure and properties of polyethylene and polypropylene as compared with the alkanes?
9. Isobutylene is polymerized into a high-molecular substance, polyisobutylene. Write the equation for the polymerization of isobutylene.

## 3.5 Diene Hydrocarbons

Structure and Nomenclature. There are hydrocarbons with two carbon to carbon double bonds, i.e. compounds that are more unsaturated than the ethylene series hydrocarbons. Since the presence of one double bond in a molecule is denoted by the ending *-ene*, hydrocarbons with two double bonds are called *dienes*, e.g. butadiene $CH_2{=}CH{-}CH{=}CH_2$. The general formula of the dienes is $C_nH_{2n-2}$.

The arrangement of the double bonds in these compounds can be different:

$\overset{1}{C}H_2{=}\overset{2}{C}{=}\overset{3}{C}H{-}\overset{4}{C}H_2{-}\overset{5}{C}H_3$

Pentadiene-1,2

$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H{-}\overset{5}{C}H_3$

Pentadiene-1,3

$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2{-}\overset{4}{C}H{=}\overset{5}{C}H_2$

Pentadiene-1,4

$\overset{1}{C}H_3{-}\overset{2}{C}H{=}\overset{3}{C}{=}\overset{4}{C}H{-}\overset{5}{C}H_3$

Pentadiene-2,3

Dienes in which the double bonds are separated by a single bond are of practical interest. The most important of them are: butadiene-1,3 (or divinyl) $CH_2{=}CH{-}CH{=}CH_2$, which is a gas easily liquefiable at $-5\,^{\circ}C$ (Fig. 20), and 2-methylbutadiene-1,3 (or isoprene) $CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}CH{=}CH_2$, which is a volatile liquid.

Chemical Properties. Since diene hydrocarbons have double bonds, they enter ordinary addition reactions, for example, they discolour bromine water, add hydrogen halides, etc. But the addition reactions here are specific. When butadiene reacts with bromine or hydrogen halide, its molecule is attached at the ends of the molecule and not at a double bond site. This can be shown as this:

$$CH_2{=}CH{-}CH{=}CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\overset{\displaystyle |}{CH_2}}{-}CH{-}CH{-}\underset{\displaystyle Br}{\overset{\displaystyle |}{CH_2}}$$

Free valencies of the second and third carbon atoms join together to form

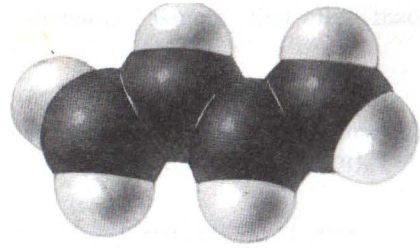


Fig. 20. A model of a butadiene molecule

a double bond in the middle of the molecule:

$$\begin{matrix} CH_2 & & & & CH_2 \\ | & & & & | \\ Br & & & & Br \end{matrix} \quad -CH=CH-$$

If bromine is present in sufficient quantity, the butadiene molecule can add another molecule of the halogen at the newly formed double bond. Write down the equation for this reaction.

Because of the presence of the double bonds, diene hydrocarbons are easily polymerized. Polymerization of dienes is used for the synthesis of rubber.

1. Draw an electron formula of isoprene.
2. How can butadiene-1,3 be prepared from (a) butane, (b) butene-1? Give the reaction equations.
3. What substances can be obtained by the hydrogenation of butadiene-1,3? Write down the reaction equations.
4. Butadiene $CH_2=CH-CH=CH_2$ is called divinyl. Can this name be given to the butadiene of the structure $CH_2=C=CH-CH_3$? Explain your answer. Name this compound in accordance with the IUPAC system.
5. Draw the structural formulas for the possible isomers of isoprene $C_5H_8$.
6. Name the substances obtained by the addition of (a) a bromine molecule, (b) one molecule of hydrogen bromide, and (c) two bromine molecules to a molecule of butadiene.
7. What maximum quantity, in grams, of bromine can react with 1.12 litres of butadiene (at STP)?

## 3.6 Rubber

Natural Rubber. Properties of Rubber. Natural rubber is derived from the milky sap of some plants, especially *Hevea Brasiliensis* (native of Brazil).

Special cuts are made in rubber trees from which the sap (latex) drips into a receptacle. The latex is a colloidal solution of rubber.

The sap is then collected and coagulated by the action of an electrolyte (e.g. acid solution) or by heating. Rubber precipitates during this coagulation.

The most important property of rubber is its *elasticity*, i.e. the property to change its shape and size under the action of comparatively slight forces (for

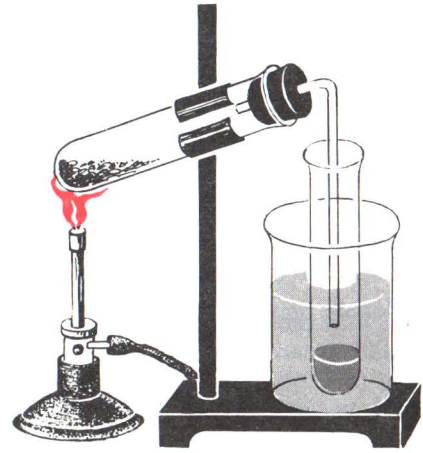


Fig. 21. Thermal decomposition of rubber

example, to be stretched or compressed) and then to recover its original configuration when the forces are removed.

Another important property of rubber is its impermeability to water and gas.

Rubber articles came in use in Europe in the early 19th century (overshoes, water proof coats, etc.). But these articles were only useful at moderate temperatures. In a hot weather they became soft and sticky, while in a very cold weather, they were hard and brittle. This disadvantage of otherwise valuable natural material was overcome by the discovery of vulcanization (or curing) of rubber.

When rubber is heated with sulphur, its elastic properties are improved. Cured rubber is stronger and more resistant to temperature changes than natural rubber.

The practical uses of cured rubber were very soon appreciated and it is now difficult to imagine a branch of industry or everyday life without goods made of cured rubber. Most rubber is used today for the manufacture of tyres for trucks, cars, airplanes, bicycles, etc. Cured rubber is used for the manufacture of drive belts, conveyor belts, hoses, electrical insulation, footwear, etc. The importance of rubber ranks that of steel, petroleum, and coal.

Composition and Structure of Natural Rubber. A qualitative analysis shows that rubber consists of two chemical elements, viz. carbon and hydrogen, in other words, rubber is a hydrocarbon.

A quantitative analysis shows that rubber has a simple formula $C_5H_8$. Its molecular weight is 150 000–500 000. Hence, rubber is a natural polymer with the molecular formula $(C_5H_8)_n$.

In order to understand better the structure of this substance, let us decompose its macromolecules. Heat a sample of rubber in a test tube as shown in Fig. 21. The sample will soon be destroyed and the liquid products of its decomposition will be collected in a receptacle. Using bromine water, we can identify that the products are unsaturated hydrocarbons. The main product of rubber decomposition is a hydrocarbon with the same molecular formula as

that of rubber. This is isoprene, a representative of diene hydrocarbons: $CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2$. One can therefore assume that the macromolecules of rubber are composed of isoprene molecules. Let us imagine how rubber is formed from isoprene molecules (disregarding the initiator). Two isoprene molecules are first united:

$$CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2+CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2\longrightarrow$$

$$\longrightarrow -CH_2-\underset{\displaystyle CH_3}{\overset{|}{\overset{|}{C}}}-\overset{|}{CH}-CH_2-+-CH_2-\underset{\displaystyle CH_2}{\overset{|}{\overset{|}{C}}}-\overset{|}{CH}-CH_2-\longrightarrow$$

$$\longrightarrow -CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-$$

The free valencies of the middle carbon atoms join to form double bonds in the middle of the molecules which are now the repeating units of the growing chain.

Another isoprene molecule is then attached to the formed particle:

$$-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-+-CH_2-\underset{\displaystyle CH_3}{\overset{|}{\overset{|}{C}}}-\overset{|}{CH}-CH_2\longrightarrow$$

$$\longrightarrow -CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-$$

This process continues, and the structure of rubber can be expressed by the following formula:

$$(-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-)_n$$

The macromolecules of rubber are thus linear. We have already got acquainted with linear polymers but those polymers were not as elastic as rubber. How can the extraordinary elasticity of rubber be explained?

Although molecules of rubber have linear structure, their chains are not straight lines but are coiled in balls. As rubber is stretched, the molecules are uncoiled and the specimen elongates. As the stretching force is removed, the molecules assume their initial configuration and the specimen shrinks to the initial shape and size. If a piece of rubber is pulled with a great effort, the

Sergei Vasilyevich LEBEDEV
(1874–1934)

Academician Lebedev was a professor at the Academy of Military Medicine (Leningrad). He is known for his classic works on the polymerization and hydrogenation of unsaturated hydrocarbons. Lebedev developed a one-step process for the manufacture of butadiene (divinyl) from alcohol (over a mixture of dehydrating and dehydrogenating catalysts). He also worked out the method for the manufacture of artificial rubber from butadiene by polymerization in the presence of metallic sodium. He supervised the construction of the first plant for the manufacture of synthetic rubber in the Soviet Union.

molecules will straighten, and as they move relative to one another, the specimen may break.

Synthetic Rubbers. Hevea trees are cultivated in many tropical countries in order to tap natural rubber from them. But natural sources of rubber cannot meet the growing demand. This has stimulated the development of methods for synthesis of artificial rubbers, especially in countries where *Hevea Brasiliensis* does not grow and rubber must therefore be imported from other countries.

In 1932, the Soviet investigator Lebedev devised a method to produce synthetic rubber. The Soviet Union was the first to manufacture artificial rubber on an industrial scale.

In his investigations, Lebedev tried to imitate nature. Since natural rubber is a diene hydrocarbon, Lebedev used the simplest and readily available diene, butadiene $CH_2{=}CH{-}CH{=}CH_2$, which could be produced from ethyl alcohol.

Lebedev polymerized butadiene in the presence of metallic sodium as a catalyst. The simplified scheme for the synthesis of rubber can be shown as this:

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow$$

$$\longrightarrow -CH_2{-}\overset{|}{C}H{-}\overset{|}{C}H{-}CH_2- + -CH_2{-}\overset{|}{C}H{-}\overset{|}{C}H{-}CH_2 \longrightarrow$$

$$\longrightarrow -CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2 \text{—and so o}$$

The structure of butadiene (polybutadiene) rubber can thus be expressed by the formula

$$(-CH_2{-}CH{=}CH{-}CH_2-)_n$$

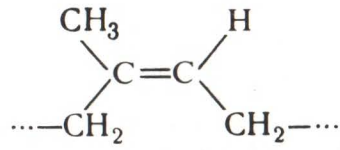
Butadiene rubber obtained by this method is impermeable to water and gas, but its elasticity and wear resistance are inferior to those of natural rubber.

Many other synthetic rubbers are now manufactured. Some of them have high mechanical strength or high chemical stability, while others are resistant to the action of solvents, etc. Each particular synthetic rubber has its own special uses.

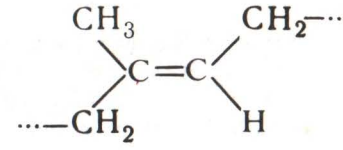
All artificially synthesized rubbers are superior to natural rubber with respect to many properties, but up till recent times they all were inferior to natural rubber with respect to elasticity. However this is the most important property of rubber as far as the manufacture of automobile and airplane tyres is concerned, because tyres undergo multiple deformations during operation.

Natural rubber is polyisoprene. The main task of investigators was therefore to synthesize artificial isoprene rubber.

Isoprene rubber was synthesized artificially, but it was still inferior to natural rubber with respect to some of its properties. The reason for this was established when the spatial structure of natural rubber was established. It was found that natural rubber has a *stereoregular* structure: the methylene groups ($CH_2$) in the structural units of the macromolecules are always arranged on one side of the double bond, i.e. they are in the *cis*-position:



*cis*-form



*trans*-form

This arrangement of the $CH_2$ groups, by which the structural units are joined in the macromolecule, promotes natural coiling of the macromolecule, which after all accounts for the high elasticity of rubber. In the case with the *trans*-position of the structural units, the macromolecules become more elongated and do not have the high elasticity.

The stereoregular structure of molecules was absent in the artificially produced rubbers, and for this reason the properties of the synthetic rubber were inferior to those of natural rubber.

The problem of obtaining artificial isoprene rubber was solved by using catalysts which gave stereoregularity to the structure of the macromolecules. Rubbers are synthesized now that are not inferior to natural rubber. Butadiene rubber with stereoregular structure of its molecules was also synthesized. To distinguish it from irregular butadiene rubber, the new rubber is called *divinyl* rubber. The stability and wear resistance of this rubber proved to be better than those of natural rubber, which makes it especially indispensable for the manufacture of tyre treads (the wearing part of the tyre).

The synthesis of artificial rubbers with stereoregular structure (isoprene and divinyl) is a remarkable achievement of the organic synthesis industry.

During Lebedev's time butadiene was synthesized from ethyl alcohol, while ethyl alcohol was produced from grain and potatoes. Manufacture of isoprene

was complicated as well. New and cheaper sources of materials for the synthesis of artificial rubbers were required. Today rubbers are synthesized from the hydrocarbons contained in petroleum gas and the products of petroleum refining.

Butadiene is prepared by the dehydrogenation of butane:

$$CH_2-CH-CH-CH_2 \longrightarrow CH_2=CH-CH=CH_2+2H_2$$

Isoprene can be prepared from isopentane (2-methylbutane):

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3 \longrightarrow CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2+2H_2$$

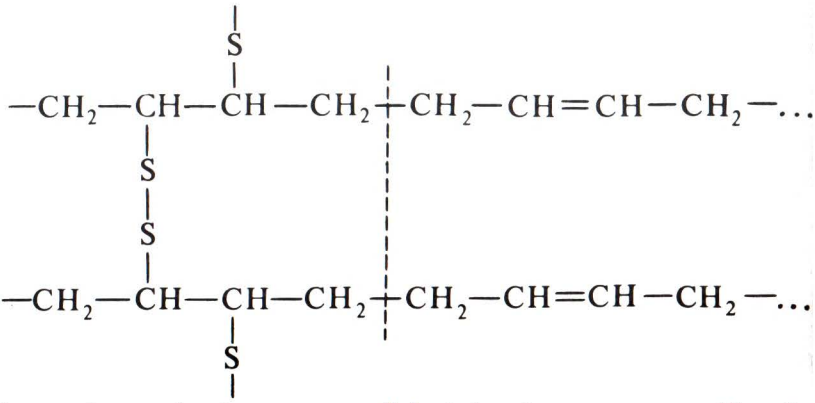
If isopentane is not available in sufficient quantities, it can be obtained by isomerizing normal pentane:

$$CH_3-CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

All these processes are catalytic. They are widely used in industry for the manufacture of monomers, which are then used for the synthesis of rubbers.

Rubber Curing. Natural and synthetic rubbers are mainly used as cured rubber, which is stronger, more elastic, and has some other valuable properties.

Mixtures of rubber, sulphur, and fillers (carbon black is the most important filler used to reinforce rubber) are moulded and then heated. The sulphur atoms react chemically with the linear molecules of rubber at some of their double bonds to cross-link them (Fig. 22). Using butadiene rubber as an example, this can be shown as this:



Many other molecules are cross-linked in the same way. Gigantic three-dimensional molecules are formed instead of linear molecules. The polymer molecules have the *spatial structure.*

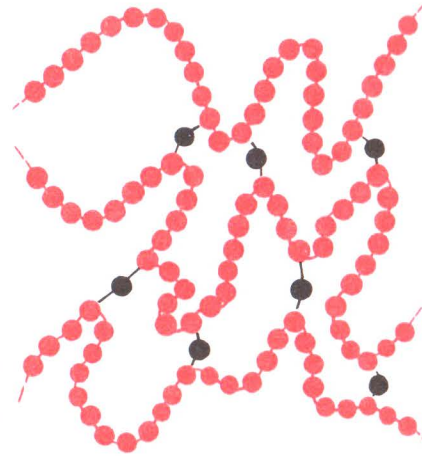


Fig. 22. Structure of cured rubber. Links of rubber macromolecules are printed in red, while the bridge atoms of sulphur in black

Rubber with a spatial structure (cured rubber) is much stronger than uncured rubber because, in addition to the ordinary intermolecular attraction forces, the forces of chemical interaction are involved. Of course, it is more difficult to separate molecules from one another in cured rubber.

The establishment of chemical bonds between the molecules accounts for the different solubilities of rubber and cured rubber. If we place samples of uncured and cured rubber in different test tubes and add petrol to both, it can be easily seen in a few days that the uncured rubber dissolves in petrol while the cured rubber only swells. Only one conclusion can be drawn from this observation: the solvent molecules can separate the molecules of the uncured rubber to dissolve it, but they fail to do so in the cured rubber.

If sulphur is added in excess of the amount required for curing normal rubber, the molecules will be cross-linked at many points during vulcanization and the cured rubber will be deprived of elasticity. The hard material thus obtained is called ebonite. It was one of the best insulating materials known before modern polymers were invented.

1. What is the difference between elasticity and plasticity? How can the elasticity of rubber be explained?
2. Prove experimentally that butadiene and isoprene rubbers are unsaturated hydrocarbons.
3. When butadiene rubber is decomposed, a hydrocarbon with the composition of $C_4H_6$ is formed. Prove that it is a diene hydrocarbon. What quantitative method should you suggest to check this conjecture?
4. Write down net equations for the polymerization of (a) butadiene, (b) isoprene. (Use the equations for the polymerization of the other polymers as a pattern.)
5. Draw the structural unit of polybutadiene in the *cis*- and *trans*-position.
6. Chloroprene rubber is obtained by the polymerization of chloroprene

$$CH_2=C(Cl)-CH=CH_2$$



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The rubber is very stable to light, heat, and solvents. Write down the equation for the polymerization of chloroprene.

7. Why is cured rubber stronger than uncured one, and why is it insoluble in organic solvents?
8. What is the difference between the structures of rubber and ebonite? Draw a diagram to illustrate your answer.

9. Carry out tests (at home) to try the attitude of uncured and cured rubbers to (a) heat, (b) petrol, (c) potassium permanganate, and compare their elasticities.
10. Use plasticine to construct a model of a fragment of a butadiene rubber molecule with a stereoregular structure.

## 3.7 Acetylene and Its Homologues (Alkyne Series)

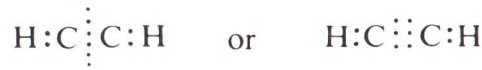
Unsaturated hydrocarbons may have bonds whose multiplicity is higher than two. Let us acquaint ourselves with another series of compounds, the simplest of which is acetylene.

Structure of Acetylene and Its Homologues. Acetylene is a colourless gas that is slightly soluble in water. Its molecular formula is $C_2H_2$.

The acetylene molecule has two hydrogen atoms less than the ethylene molecule. The third bond is therefore formed between the carbon atoms. The structural formula of acetylene is

$$H-C\equiv C-H \quad \text{or} \quad HC\equiv CH$$

The triple bond in the acetylene molecule indicates that the carbon atoms are bonded by three pairs of electrons:



Studies show that the carbon and hydrogen atoms are arranged along a straight line in the acetylene molecule. The structure of the molecule is linear. The carbon atoms are connected by one σ bond and two π bonds. Since each carbon atom is connected through σ bonds with only two other atoms (one carbon and one hydrogen), only two electron clouds are involved in hybridization: one *s* and one *p* electron cloud. This is called *sp hybridization*. These hybrid clouds are asymmetrical dumb-bells. They tend to separate from each other as far apart as possible and establish bonds with other atoms in opposite directions at an angle of 180°. The clouds of the other two *p* electrons are not involved in hybridization. They remain symmetrical dumb-bells and overlap with similar clouds of the other carbon atom to form two π bonds in two perpendicular planes (Fig. 23).

The establishment of the third bond causes the carbon atoms to come closer together and the distance between their centres is 0.120 nm. In structural models, this is expressed by a greater flattening of the balls showing the carbon atoms (Fig. 24).

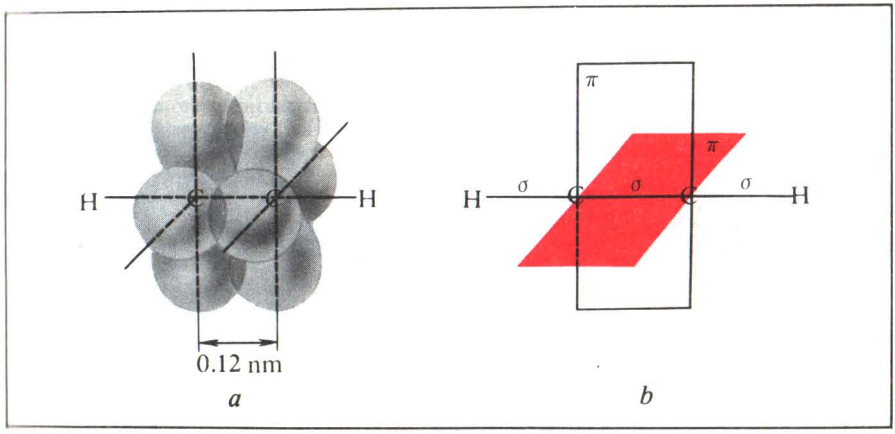



Fig. 23. Formation of π bonds in an acetylene molecule:

*a* lateral overlapping of *p* electron clouds; *b* – two mutually perpendicular planes in which π bonds are formed

Acetylene Homologues. Like methane and ethylene, acetylene begins a new homologous series. The series includes hydrocarbons with one triple bond between the carbon atoms.

According to the IUPAC system, the names of these compounds are formed by replacing the ending *-ane* in the corresponding saturated hydrocarbons by the ending *-yne*. As in the case of ethylene hydrocarbons (alkenes), the carbon atoms of the acetylene hydrocarbons (alkynes) are numbered from the end nearest the multiple (triple) bond:

$CH{\equiv}CH$ Ethyne

$\overset{1}{C}H{\equiv}\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H_3$ Butyne-1

$\overset{1}{C}H_3-\overset{2}{C}{\equiv}\overset{3}{C}-\overset{4}{C}H_3$ Butyne-2

$$\overset{1}{C}H{\equiv}\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H(\overset{|}{C}H_3)-\overset{5}{C}H_2-\overset{6}{C}H_3$$

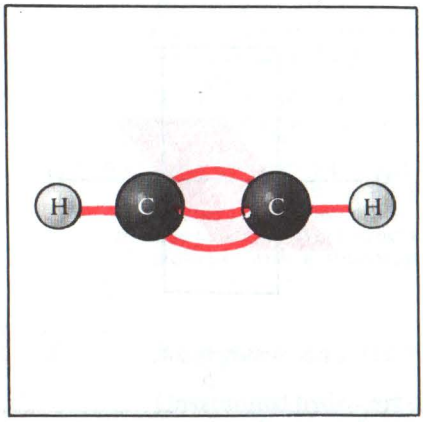
4-Methylhexyne-1

Isomerism also occurs in the acetylene homologous series. It depends on the branched carbon chains and also on the position of the triple bond. Decide if there are any isomers among the substances whose formulas are given above.

Other sorts of hydrocarbons are isomers of acetylene hydrocarbons. What substances are these? In order to answer this question, compare the general formula of the acetylene hydrocarbons (alkynes) with the general formulas of the other homologous series you know.

Chemical Properties. We shall study the properties of acetylene, because this gas is the most important substance in this series.

As distinct from methane and ethylene, acetylene (ethyne) burns with



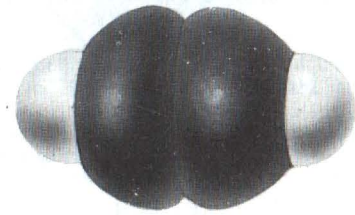



Fig. 24. Models of an acetylene molecule

a smoky flame. Explain the formation of soot by comparing the percentage compositions of the hydrocarbons.

Many of you might have seen a welder with an oxy-acetylene torch. This apparatus is used for welding and cutting metals. The flame of the burning acetylene in the torch produces no soot. Acetylene can burn with a bright flame without soot if additional air is supplied to the torch. The carbon particles become strongly heated in the middle zone of the flame giving it brightness and burning completely without soot. In an oxy-acetylene torch the air is replaced by oxygen. The acetylene burns completely to give a great deal of heat (up to 3000 °C). Mixtures of acetylene with oxygen and air are explosive.

Once we know the electron structure of acetylene we can suggest that the $\pi$ bonds here are weaker than the main $\sigma$ bond, and that oxidation and addition can occur at the bonds.

In order to decide whether acetylene is an unsaturated hydrocarbon, fill a cylinder with the gas and add potassium permanganate solution: the colour quickly vanishes to indicate that acetylene (like ethylene) is easily oxidized.

Its reaction with bromine is a characteristic addition reaction. This is another property that makes it similar to ethylene. The reaction occurs in two steps. First bromine is added at one $\pi$ bond:

$$H-C\equiv C-H + Br_2 \longrightarrow H-\underset{\displaystyle Br}{\overset{|}{C}}=\underset{\displaystyle Br}{\overset{|}{C}}-H$$

1,2-Dibromoethane

The second bromine molecule is added next:

$$H-\underset{\displaystyle Br}{\overset{|}{C}}=\underset{\displaystyle Br}{\overset{|}{C}}-H + Br_2 \longrightarrow H-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\overset{|}{C}}}-\underset{\displaystyle Br}{\overset{\displaystyle Br}{\overset{|}{C}}}-H$$

1,1,2,2-Tetrabromoethane

Once we know the mechanism of bromine addition to ethylene, we can conclude which electron processes occur in the molecule during the interaction of acetylene with bromine.

Acetylene is more unsaturated than ethylene and one might conclude that it would easier add the halogens. But this is not so. The rate of the addition reaction is slower. This fact can be explained as follows: the distance between the nuclei in the triple bond is shorter than in the double bond, and the lateral overlapping of the *p* electron clouds is therefore denser. The π bonds are thus more stable than they are in ethylene.

Hydrogen can be added to acetylene in the presence of a catalyst (platinum or nickel). The acetylene is first converted into ethylene and then into ethane:

$$CH{\equiv}CH + H_2 \rightarrow CH_2{=}CH_2$$

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$$

Acetylene can add molecules of more complex substances. When hydrogen chloride is attached to acetylene using one of its bonds (in the presence of mercuric chloride as a catalyst), a gaseous substance is formed which is known as vinyl chloride (chloroethene):

$$CH{\equiv}CH + HCl \longrightarrow CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}}$$

**Uses of Acetylene.** Acetylene is the most widely used hydrocarbon with a triple bond. Until recently, it was mainly used for metal welding and cutting, but now it is also used for the synthesis of various organic compounds.

If chlorine reacts with acetylene, a solvent, 1,1,2,2-tetrachloroethane, is obtained

$$CH{\equiv}CH + 2Cl_2 \rightarrow CHCl_2{-}CHCl_2$$

Tetrachloroethane can be further treated to yield other chlorine derivatives. If hydrogen chloride is removed, for example, trichloroethene is formed; this too is a valuable solvent and is used for dry cleaning:

$$H{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle [Cl}{\overset{|}{C}}}}}{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle H]}{\overset{|}{C}}}}{-}Cl \longrightarrow CHCl{=}CCl_2 + HCl$$

1,1,2-Trichloroethene

Large quantities of acetylene are used in the manufacture of chloroethene (vinyl chloride), which is polymerized into polyvinyl chloride (PVC):

$$n\,CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow \left(-CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}-\right)_n$$

Polyvinyl chloride is widely used as an electrical insulator and for making overcoats, table cloths, artificial leather, and pipes.

Acetylene is also used for the manufacture of other polymers which are raw materials for the production of many plastics, rubber, and synthetic fibre.

Acetylene is also used for the manufacture of acetic acid.

Preparing Acetylene. Both in the laboratory and in industry, acetylene was mostly produced from calcium carbide. If lumps of calcium carbide are placed in water (or water is poured on calcium carbide) acetylene is liberated vigorously

$$CaC_2 + 2HOH \rightarrow C_2H_2 + Ca(OH)_2$$

However, this method could not meet the growing demand for acetylene (especially the demand of polymer materials production) because a great deal of electricity is required to prepare the calcium carbide.

Calcium carbide is prepared in electric furnaces by the reaction between carbon (coke or anthracite) and lime at a temperature of 2000 °C:

$$CaO + 3C \rightarrow CaC_2 + CO$$

Now acetylene is mostly produced from natural gas (methane). If methane is heated to high temperatures, it decomposes into carbon and hydrogen. However, one of the intermediate of this reaction is acetylene:

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$
$$C_2H_2 \rightarrow 2C + H_2$$

$$2CH_4 \rightarrow 2C + 4H_2$$

The main problem is the separation of acetylene at the intermediate stage before it decomposes into carbon and hydrogen. This can be done if the acetylene is quickly removed from the reaction system and cooled. There is another advantage in this process: high temperatures are required to decompose methane; but methane itself may be used as the source of the required heat. Part of the methane thus burns as a fuel, while the other part is used to obtain the desired product. This process can be realized as shown in Appendix, Fig. I.

Preheated methane and oxygen (2 : 1) are rapidly fed into a cylindrical reaction vessel lined with fire brick. The gases are mixed in a special chamber and delivered into the reaction space through narrow channels. Part of methane burns here to raise the temperature to about 1500 °C, while the rest of the methane decomposes into acetylene and hydrogen.

The gases are delivered extremely rapidly so that the reaction products only stay in the high-temperature zone for a thousandth of a second. The reaction products are then quickly cooled with water.

In addition to acetylene and hydrogen, the reaction products also include soot (gas black), carbon oxides, and some other substances. The soot is washed out with water, and acetylene is then isolated from the mixture of reaction products. The hydrogen produced in this reaction can be used for ammonia synthesis and for preparing other organic compounds.

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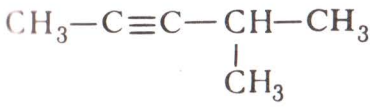
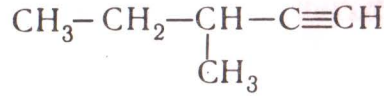
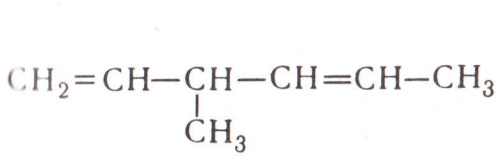
? 1. What are the relative densities of ethane, ethene, and ethyne? (Do not calculate their molecular weights.)

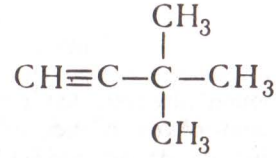
△ 2. Decide if a branched hydrocarbon may exist with four carbon atoms and a triple bond? Explain your answer.

3. Give the structural formula of a substance which is an isomer of butyne, but which belongs to another series of hydrocarbons.
4. Using the IUPAC system, name the following substances

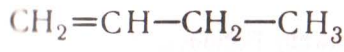


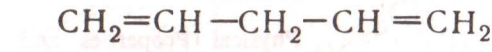


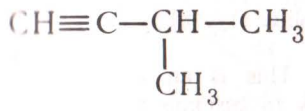


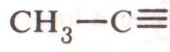


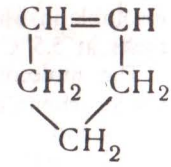
5. Which of the substances given below are (a) homologues, (b) isomers of a substance with the structure $CH{\equiv}C{-}CH_2{-}CH_2{-}CH_3$?











6. Is *cis-trans* isomerism possible with acetylene hydrocarbons?
7. Write an equation for the addition reaction of hydrogen bromide to propyne (the first stage); use the Markownikoff rule. Explain your answer. Name the substance formed.
8. Write down the equation for complete combustion of acetylene, and calculate the volume of oxygen (at STP) which is needed to burn 13 g of acetylene.
9. What is the maximum quantity of bromine, in grams, that can react with 11.2 g of acetylene?
10. How can chloroethane be obtained from acetylene? Write down the reaction equations.
11. Write down the equations of the reactions by which 1,2-dichloroethane is produced from acetylene.
12. What volume of acetylene (at STP) can be obtained from 1 kg of commercial calcium carbide (containing 30 per cent of impurities)?
13. What do you know about halogen substituted hydrocarbons? Write down their names, formulas, and indicate their properties and uses.

# 4 Aromatic Hydrocarbons

This group of hydrocarbons was so named because of the fragrance that was characteristic of the first known representatives. Later it was found, however, that most of the substances belonging to this group from the point of view of their structure and chemical properties, have no aromaticity But the name survived.

The simplest representative of aromatic hydrocarbons is benzene.

## 4.1 Benzene

**Physical Properties and Structural Formula.** Benzene is a low-boiling colourless liquid with a specific odour and is insoluble in water. When cooled it freezes into a white crystalline mass that melts at 5.5 °C.

The molecular formula of benzene is $C_6H_6$. This is an unsaturated hydrocarbon: its molecule needs eight hydrogens to become a saturated compound.

If benzene is shaken with bromine water or potassium permanganate solution, the result is surprising: the reaction specific for unsaturated compounds is absent. The explanation can be found in the structure of benzene.

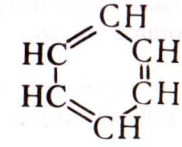
The structure of benzene becomes clear when we study the synthesis of benzene. Benzene can be obtained by passing acetylene through activated carbon at a temperature of 650 °C.

A comparison of the molecules of acetylene and benzene ($C_2H_2$ and $C_6H_6$, respectively) indicates that three molecules of acetylene form one molecule of benzene, i.e. a polymerization (trimerization) reaction takes place:

$$3C_2H_2 \rightarrow C_6H_6$$

But this fact is not decisive for any conclusion on the structure of benzene because we do not know in what way the acetylene molecules combine into a benzene molecule. Both linear and cyclic structures with the formula of $C_6H_6$ may be imagined, e.g.:

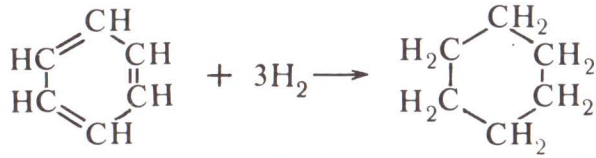
$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$



The chemical properties of the substance should therefore be examined. If

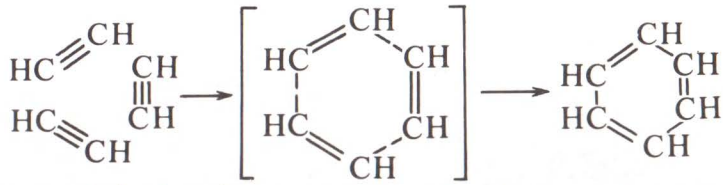
a mixture of benzene and hydrogen is passed through a heated tube with a catalyst, three hydrogen molecules are added to each benzene molecule to give cyclohexane, whose structure is well known to us.

The formation of cyclohexane can only be understood on the assumption that the initial substance too has a cyclic structure:



In fact, if benzene had an open chain of carbon atoms, four rather than three hydrogen molecules would be needed to completely saturate the benzene molecule ($C_6H_6 + 4H_2 \rightarrow C_6H_{14}$), but this contradicts experience.

The formation of a cyclic molecule of benzene from three acetylene molecules can be shown as this:



Thus we can conclude that the structural formula of benzene is cyclic.

The above structural formula was suggested by the German investigator Kekulé (1865) and is still used by chemists although it is not completely satisfactory.

We have established experimentally that benzene does not react with bromine water or potassium permanganate solution, although its molecule (as suggested by the formula) has three double bonds. This contradiction was solved by a deeper study of its structure – the character of bonds between the atoms in the molecule.

Electron Structure of Benzene. It has been established by modern physical methods that the molecule of benzene has a cyclic structure and that all six carbon atoms lie in the same plane. Kekulé's formula was thus proved experimentally, but it was still necessary to establish the mode in which the atoms are connected in the benzene molecule.

The studies showed that the distances between all the carbon atoms in the benzene molecule are 0.140 nm. This indicates that benzene has neither single nor double bonds because the interatomic distance should then be either 0.154 nm or 0.134 nm, respectively. The electron theory explains this phenomenon.

All the carbon atoms in the benzene molecule are in the state of $sp^2$ *hybridization*. Three hybrid electron clouds of each carbon atom (elongated dumb-bells) form two σ bonds with the neighbouring carbon atoms and one σ bond with the hydrogen atom in the plane of the ring; it is evident that the angles between these three bonds are 120° (Fig. 25). The clouds of the fourth

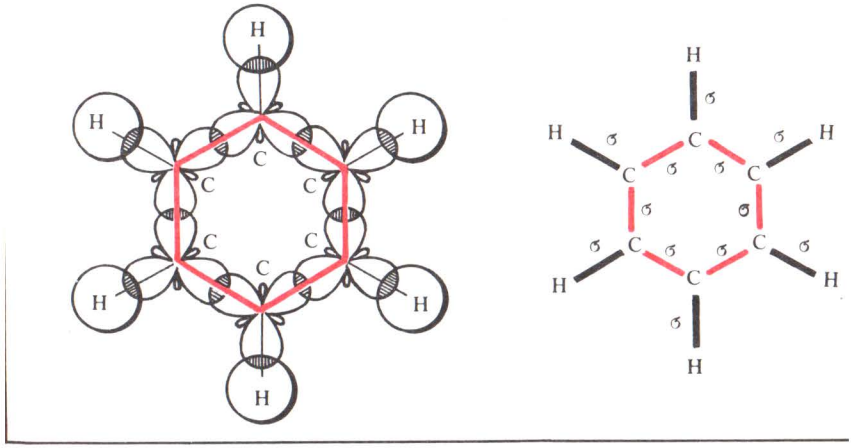


Fig. 25. Formation of σ bonds in a molecule of benzene

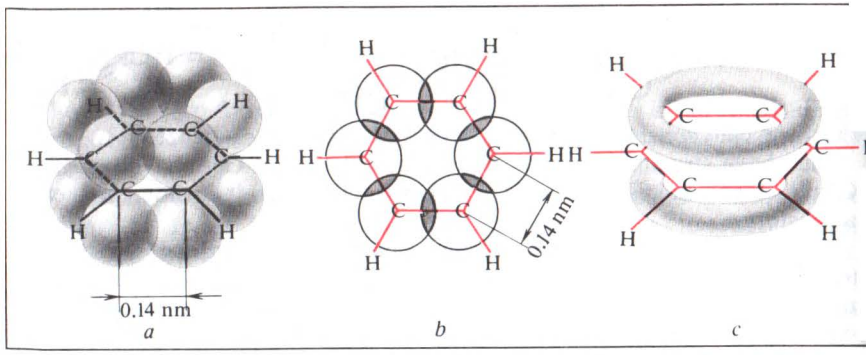



Fig. 26. Formation of π bonds in a molecule of benzene:

*a-b* – lateral overlapping of *p* electron clouds in two projections; *c* – distribution of electron density of molecular π cloud above and below the plane of the atomic nuclei

electrons that are not involved in the hybridization and retain the shape of symmetrical dumb-bells are perpendicular to the plane of the σ bonds. Each cloud is equally overlapped by the electron clouds of the neighbouring carbon atoms (Fig. 26*a*). If the molecule is projected on a plane, these electron clouds would appear as overlapping circles (Fig. 26*b*). A single system of six π electrons common for all the carbon atoms (Fig. 26*c*), is formed instead of three separate π bonds. The distances between the carbon atoms are decreased under the action of this common π electron cloud from 0.154 to 0.140 nm. The structural model of the benzene molecule is shown in Fig. 27.

Since the electron density is distributed evenly throughout the molecule, all the bonds between the carbon atoms are equal.

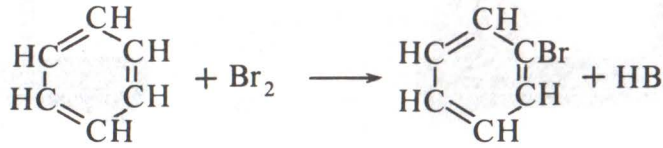
In order to show the even distribution of electron density in the benzene

molecule, its structural formula is often shown as a hexagon with a circle inside it, although the Kekulé formula is still used

Chemical Properties. Like all hydrocarbons, benzene is flammable. Much soot is formed during combustion of benzene, because the proportion of carbon in it is as high as that in acetylene.

As we already know, benzene does not react with bromine water. But under different conditions it can react with bromine.

Assemble the apparatus as shown in Fig. 28, using a long vertical tube as a condenser. Place a small quantity of benzene into the flask, and add bromine and iron chips. The iron is needed to form a catalyst $FeBr_3$. The orifice of the tube soon begins fuming. Dissolve the evolving gas in water. Now add a small quantity of silver nitrate to make sure that bromine reacts with benzene to give hydrogen bromide HBr. A heavy liquid remains in the flask. This is bromobenzene $C_6H_5Br$. The bromination of benzene can be expressed by the equation




Bromobenzene

It can be seen that bromine substitutes one of the hydrogen atoms.

The mechanism of this reaction differs from that of the substitution reactions of saturated hydrocarbons. It does not occur through formation of free radicals, nor is it a chain reaction. Under the catalyzing action of the ferric bromide $FeBr_3$ the bromine is polarized $Br^{\delta+} : Br^{\delta-}$. The positively charged bromine is attracted by the six-electron

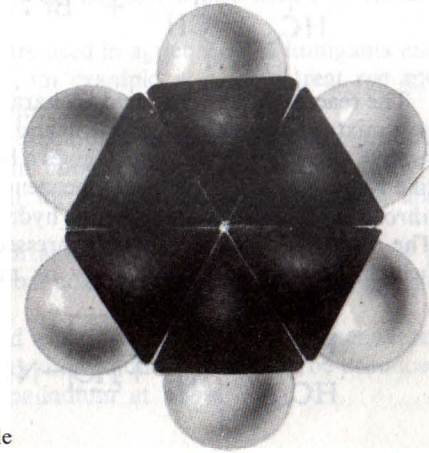


Fig. 27. A model of the benzene molecule

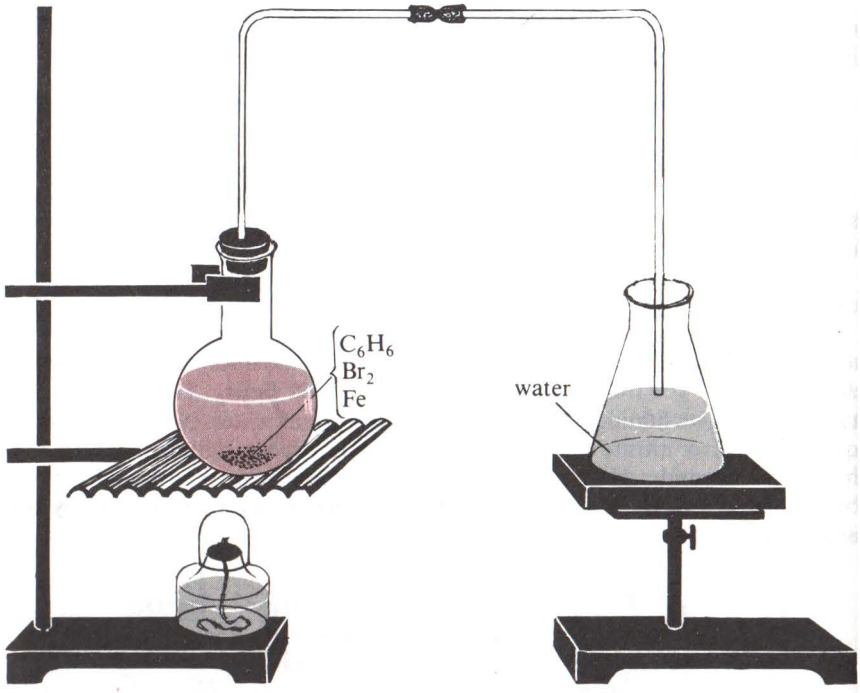
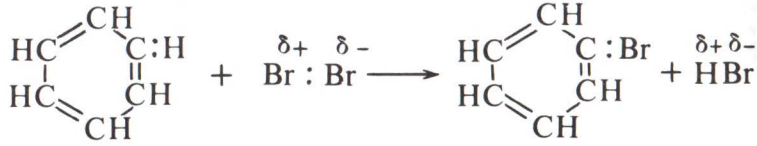
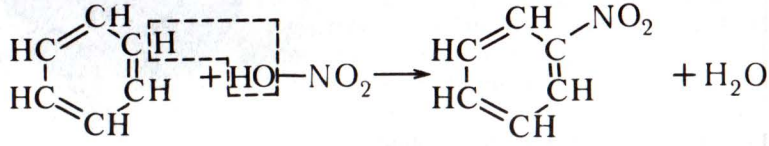



Fig. 28. Bromination of benzene

cloud of the benzene molecule to establish a covalent bond with one of its carbon atoms displacing one of the hydrogens as a proton. The negatively charged bromide ion interacts with the proton to form a molecule of hydrogen bromide:



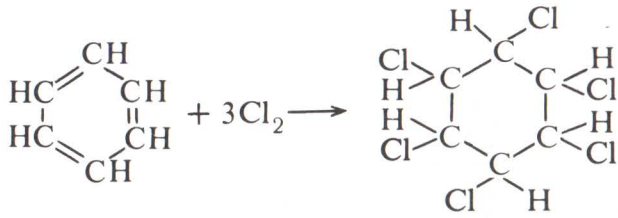

The reaction with nitric acid is characteristic of benzene. If benzene is added to a mixture of concentrated nitric and sulphuric acids and the flask is slightly heated, a reaction occurs which gives a heavy yellowish liquid that has an odour like bitter almond. This is nitrobenzene $C_6H_5—NO_2$. The $—NO_2$ group (the *nitro group*) substitutes here for the hydrogen atom like in the previous reaction. The nitration reaction can be expressed by the following chemical equation (which, however, does not show its mechanism):



Although an unsaturated compound, benzene is similar to the saturated hydrocarbons as regards its ability to take part in substitution reactions.

Benzene can also enter addition reactions under certain conditions. We already know one such reaction: benzene can add hydrogen. Write down the equation for this reaction using ordinary molecular formulas.

Chlorine can also be added to benzene if a mixture of these two substances is exposed to light. The reaction yields hexachlorocyclohexane, a crystalline substance:



The fact that benzene can enter addition reactions with hydrogen and chlorine indicates that benzene has some properties in common with unsaturated hydrocarbons as well.

The chemical properties of benzene are intermediate between saturated and unsaturated hydrocarbons. Benzene enters reactions characteristic of hydrocarbons of both types, but it enters substitution reactions more readily than saturated hydrocarbons and enters addition reactions less readily than unsaturated hydrocarbons. This characteristics of benzene is due to its electronic structure.

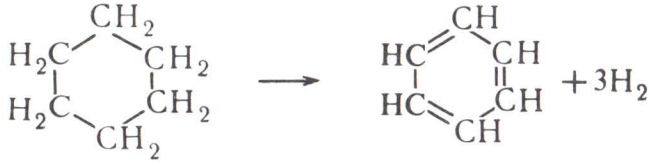
Uses of Benzene. Benzene is the starting material for the manufacture of many organic compounds. The nitration of benzene gives nitrobenzene $C_6H_5NO_2$, while its chlorination yields the solvent chlorobenzene $C_6H_5Cl$ and other chlorine derivatives. Benzene is used as the starting material for the synthesis of medicinal preparations, perfumery, various dyes, and monomers for the synthesis of high-molecular compounds. Benzene is also used as a solvent and an additive to motor fuels.

The chlorine derivatives of benzene are used in agriculture as fumigants and insecticides, hexachlorobenzene $C_6Cl_6$, for example, is used to treat rye and wheat seeds to protect them from smut.

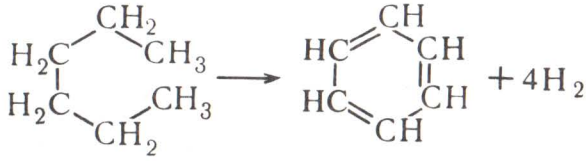
An important halogen derivative is hexachlorobutadiene $C_4Cl_6$ (the product of chlorine substitution for hydrogen in butadiene-1,3). This is used to fight phylloxera of grapes. Draw structural formulas of hexachlorobenzene and hexachlorobutadiene.

Preparing Benzene. Coal is an important source of benzene. When coal is strongly heated in the absence of air (coal coking), many volatile products are formed, one of which is benzene.

The Soviet investigators have devised a method for obtaining benzene from non-aromatic hydrocarbons. N. Zelinsky showed that benzene can be produced from cyclohexane over platinum or palladium at about 300 °C:



It was also established that heating *n*-hexane over a suitable catalyst can also yield benzene (dehydrocyclization):



Preparing benzene from saturated hydrocarbons and cycloparaffins is very important since the demand for benzene is increasing.

? 1. What contradiction exists between the structural formula of Kekulé and the properties of benzene, and how does the electron theory reconcile this contradiction?

△ 2. The structural formula of benzene is sometimes shown as a hexagon with a circle inside it. What does, in your opinion, the circle represent?

3. How can benzene $C_6H_6$, hexane $C_6H_{14}$ and hexene $C_6H_{12}$ be identified by their chemical properties?

4. Give examples of reactions showing the similarity between benzene and (a) saturated, (b) unsaturated hydrocarbons. What are the differences in their properties?

5. When we studied inorganic chemistry, we discussed substitution reactions, in which the reactants and the resultant products are a simple substance and a compound. During the nitration of benzene, two composite substances enter the reaction and the resultant products are also two compounds. Why is benzene nitration regarded as a substitution reaction in organic chemistry? What is the main sign of substitution reaction?

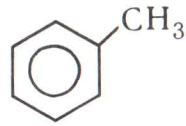
6. When we discussed the reactions of benzene, there were two which proceed in opposite direction. What are these reactions? Express them by one equation and specify the conditions under which the process can be carried out in a desired direction.

7. How can benzene be prepared from methane? Write out the reaction equations and specify the conditions under which they can be realized.

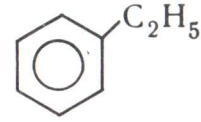
## 4.2 Benzene Homologues

Structure of Benzene Homologues. Like other hydrocarbons, benzene is the simplest in its homologous series. Its homologues can be regarded as substituted benzenes, i.e. the products of substitution of various hydrocarbon radicals for one or several hydrogen atoms. If we show the common π electron system as a circle, and omit the hydrogen symbols in the benzene ring (a common practice), the formulas of the next homologues will be

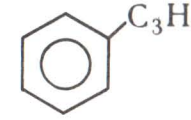
as follows:



Methylbenzene



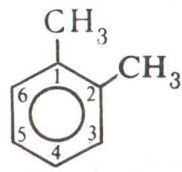
Ethylbenzene



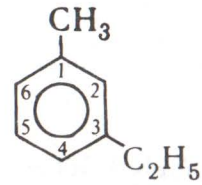
Propylbenzene

Compare these compounds and make sure that the homologous difference here is the same $CH_2$.

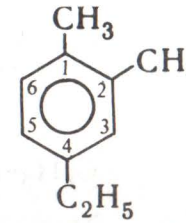
In naming substances whose molecules contain the benzene ring with several additional radicals, the carbon atoms are given numbers, which are then used to indicate the positions of the groups in substituted benzenes, e.g.:



1,2-Dimethylbenzene



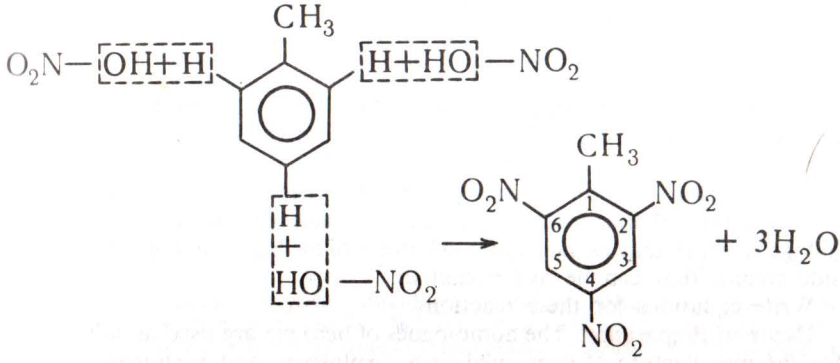
1-Methyl-3-ethylbenzene



1,2-Dimethyl-4-ethylbenzene

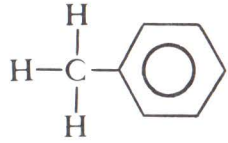
Chemical Properties of Benzene Homologues. Substituted benzenes have much in common with the parent benzene as regards their properties. Consider a few examples.

Three nitro groups can be introduced into the benzene and toluene molecule $C_6H_5—CH_3$ by nitration. It appears that toluene is nitrated more easily than benzene. The product of toluene nitration is 2,4,6-trinitrotoluene, the explosive known commonly as TNT:



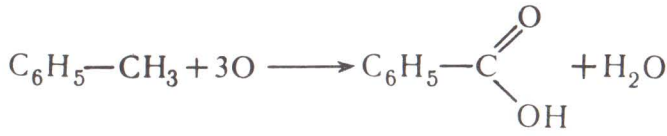
The higher reactivity of the benzene ring in the 2, 4 and 6 positions is explained by the effect of the $—CH_3$ radical. This example illustrates the effect atoms have on one another.

Toluene can be regarded not only as a substituted benzene (the hydrogen atom is replaced by the methyl group), but also as methane in which the aromatic radical $C_6H_5$— (phenyl) substitutes for the hydrogen:



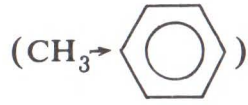
Methane is very stable to oxidants, but if potassium permanganate solution is added to toluene and heated, the violet colour gradually disappears, because the $-CH_3$ group in the toluene is oxidized.

As potassium permanganate acts on toluene, the methyl group is oxidized to the carboxyl group to form benzoic acid. If we replace (as is conventional) the oxidant by oxygen atoms, this reaction can be expressed as



We can thus see that while the methyl group in toluene affects the benzene ring facilitating substitution reactions (at positions 2, 4 and 6), the benzene ring affects the methyl group to decrease its stability to oxidants.

This phenomenon is due to effects the electron structures have on each other. The increased reactivity of the benzene ring can, in a general form, be explained as follows. The methyl group displaces the bond electrons (remember the Markownikoff rule). Being a part of toluene, the methyl group shifts the electron pair in the direction of the benzene ring



This upsets the even distribution of the π electron cloud. The electron density increases at positions 2, 4, 6 to make them more vulnerable to the attack of substitutes.

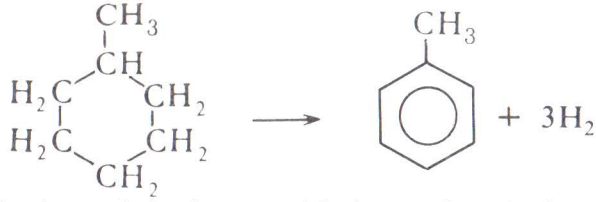
In addition to nitration reactions, aromatic hydrocarbons can participate in other reactions characteristic of benzene. They can react, for example, with the halogens (which may replace hydrogen atoms of the benzene ring or those of the side chain); they can be hydrogenated.

Write equations for these reactions.

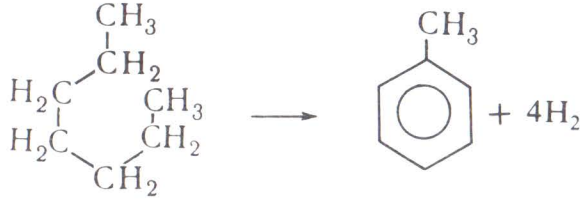
Uses and Preparation. The homologues of benzene are used as solvents and for the manufacture of dyes, medicines, explosives, and perfumes. They are obtained from the products of coal coking, and like benzene from the paraffins and cycloparaffins (the homologues of cyclohexane).

Toluene, for example, can be obtained by dehydrogenation of methyl-

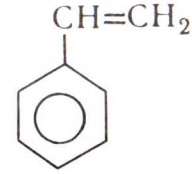
cyclohexane:



or by cyclization and simultaneous dehydrogenation of *n*-heptane:



1. Derive the general formula for benzene homologues.
2. A hydrocarbon has the formula $C_7H_8$. It does not discolour bromine water, but is hydrogenated to give methylcyclohexane. Write the structural formula of this hydrocarbon.
3. Write down the structural formulas of aromatic hydrocarbons isomeric to propylbenzene and name them.
4. The polymerization (trimerization) of propyne $CH{\equiv}C{-}CH_3$ gives a substituted benzene. Write down the reaction equation and name the substance.
5. Depending on conditions, toluene reacts with bromine to substitute bromine for the hydrogens either in the ring or in the methyl group. In what direction will the reaction proceed (a) in the presence of a catalyst, (b) if the mixture is exposed to light? Explain your answer.
6. What volume of hydrogen (at STP) is formed during the conversion of 200 g of heptane into toluene? Compare it to the volume of hydrogen that is liberated during the conversion of the same quantity of hexane into benzene.
7. Ethylcyclohexane can be converted into an aromatic hydrocarbon by dehydrogenation. What is this hydrocarbon? Write down the reaction equation.
8. Benzene can have derivatives not only with saturated, but also with unsaturated side chains. The simplest is styrene



(liquid). Stryrene discolours bromine water and potassium permanganate solution. Write down the equation for its reaction with bromine water. Is styrene a homologue of benzene? A derivative of which other hydrocarbon can styrene be considered to be?
9. Styrene (see the previous item) can polymerize like ethylene to give a thermoplastic polymer known as polystyrene. Write down the reaction of styrene polymerization.



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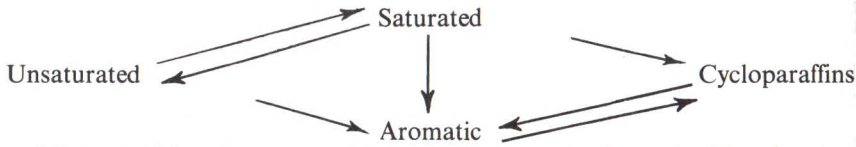
## 4.3 Hydrocarbon Variety. Relations Between Homologous Series

We have got acquainted with several groups of hydrocarbons. But these examples do not cover the great variety of hydrocarbons. Unsaturated hydrocarbons, for example, may contain several double bonds and several triple bonds, and there are also hydrocarbons whose molecules contain both double and triple bonds. Aromatic compounds may have several benzene rings in their molecules.

Using hydrocarbons as example, one can now understand how many compounds can be formed by only two chemical elements. And we know how to explain this phenomenon. It depends, in the first instance, on the property of carbon atoms to combine in normal and branched chains, to form cycles, and to establish bonds, single, double, and triple. We also know that hydrocarbons can form series of homologues and isomers.

Another conclusion we must make from what we have learnt is that all the homologous series we have discussed are not independent but are closely related and can be converted into one another. Saturated hydrocarbons can be converted into unsaturated ones, cycloparaffins can be transformed into aromatic compounds, unsaturated hydrocarbons can be turned into saturated hydrocarbons, etc.

The conversions of some homologues into others can be represented in the following diagram:




Other transitions from one series to another can also be realized by chemical methods, but are not shown in the diagram. The Soviet academician Zelinsky and his students made an important contribution to the study of the mutual conversions of hydrocarbons.

△ ?

1. Assign the following hydrocarbons to their homologous series:

$$C_6H_5{-}C_3H_7, C_6H_{14}, C_6H_6, C_4H_{10}$$

$$CH_3{-}CH{=}CH{-}CH_3, C_6H_4{<}^{CH_3}_{CH_3} \qquad HC{\equiv}C{-}CH_3$$

2. Give the general formulas of the homologous series that you know. Given the same number of atoms, homologues of which series are isomers?
3. What types of isomerism do you know? Give examples.
4. What types of electron cloud hybridization do you know? Give examples of the corresponding substances. In what way does hybridization affect the direction of chemical bonds of a carbon atom?
5. What chemical properties are characteristic of hydrocarbons containing (a) single bonds, (b) multiple bonds, and (c) aromatic rings? Illustrate your answer by the appropriate reaction equations.

Nikolai Dmitrievich ZELINSKY
(1861–1953)

Zelinsky was a professor at Moscow University, an academician, and a Hero of Socialist Labour. He was the founder of the largest school of organic chemists in the Soviet Union. Zelinsky synthesized many hydrocarbons and other organic compounds. He discovered the catalytic conversion of cycloparaffins into aromatic hydrocarbons, catalytic cracking of petroleum hydrocarbons. He synthesized benzene from acetylene over activated carbon. Zelinsky was a pioneer of the modern theory of catalysis and studied the chemistry of proteins. He was the inventor of the general purpose gas mask.

6. Give equations for reactions which illustrate the conversions of hydrocarbons as indicated in the diagram.
7. Write the equations for the reactions which prove that various hydrocarbons (paraffins, cycloparaffins, unsaturated, and aromatic) may be produced from carbon and hydrogen. Under what conditions can these reactions be realized?

# 5 Natural Sources of Hydrocarbons

The hydrocarbons we have discussed in previous chapters are important not only as compounds that can be used as examples for the discussion of the main theoretical problems of organic chemistry, but also as materials of major economic importance. They are used as starting materials for the manufacture of almost all products of organic synthesis and as fuels.

The most important sources of hydrocarbons are natural gas (marsh gas or oil gas), petroleum, and coal.

## 5.1 Natural and Oil Gases

Natural Gas. We have already got acquainted with natural gas. When we studied methane we mentioned that it is the major component of natural gas. In addition to methane, natural gas also contains its nearest homologues: ethane, propane, and butane. The higher the molecular weight of the hydrocarbon, the lower its content in natural gas. The average composition of natural gas is (in per cent by volume): $CH_4$ 80-97, $C_2H_6$ 0.5-4, $C_3H_8$ 0.2-1.5, $C_4H_{10}$ 0.1-1.0, $C_5H_{12}$ 0-1, and $N_2$ and other gases 2-13.

The main advantage of natural gas over solid and liquid fuels, and also over other gases (coke gas, blast-furnace gas) is its very high heat of combustion.

Natural gas is used in industry both as a boiler fuel, and as a fuel for open-hearth and blast furnaces, in glass making, etc. Using natural gas as the fuel in blast furnaces saves coal, decreases the sulphur content in the pig iron, and significantly increases the productivity of the furnace.

Natural gas is an important raw material in the chemical industry: methane is used for the manufacture of hydrogen, acetylene, gas black, and various chlorine derivatives.

Oil (Petroleum) Gas. Oil gas is also a natural gas, but it has a different name because it accompanies petroleum. It is dissolved in petroleum and collects in large quantity over the petroleum. Under the pressure of the gas, the petroleum is pushed out from its deposit to the surface through a drilled hole. When the pressure is lowered, the gas is easily separated from the petroleum.

The oil gas was once not used and was first burnt at the site of petroleum recovery. Now this gas is used as a valuable raw material in chemical industry. In addition to methane, oil gas contains considerable quantities of other hydrocarbons, such as ethane, propane, butane, pentane, which are now recovered from oil gas in larger quantities than from natural gas. For a more rational use of oil gas, it is separated into mixtures of a narrower composition.

A mixture of pentane, hexane, and other hydrocarbons that are liquids under normal conditions (they are partly evaporated from petroleum with gases) is the so-called *wet gas* (casing-head or natural gasoline). *A mixture of propane and butane* is then separated. What remains after the separation of wet gas, is called *dry gas* and consists mainly of methane and ethane.

Natural gasoline contains volatile liquid hydrocarbons and is used as an additive to petrols to facilitate ignition during engine starting. Propane and butane are liquefied and used as high-calorie gaseous fuel. The composition of dry gas is similar to natural gas, and it is therefore used for the manufacture of acetylene, hydrogen, and other substances. It is also used as fuel.

Some individual hydrocarbons are separated from oil gas. These include ethane, propane, and *n*-butane. They are used for making unsaturated hydrocarbons. Try to remember which reactions are involved.

1. Write down the equations for the reactions by which hydrogen, gas black, acetylene, and chlorine derivatives can be obtained from natural gas (methane).
2. What products are isolated from oil gas and what are their uses?
3. Explain why natural gasoline ignites in an engine more easily than normal petrol?
4. Give several equations to show the possible chemical uses of butane contained in oil gas.

## 5.2 Petroleum. Petroleum Products

Physical Properties and Composition of Petroleum. Petroleum is a dark oily combustible liquid with a characteristic odour. It is slightly lighter than water, in which it does not dissolve.

One can easily prove experimentally that petroleum is a mixture of hydrocarbons. If a sample of petroleum is heated in a flask (see Fig. 29), it can be seen that petroleum is not distilled at a definite temperature like individual substances. Petroleum distills within a wide temperature range. The substances with low molecular weights are first distilled at moderate heating. As the temperature rises, substances with higher molecular weights (boiling at higher temperatures) are distilled.

The composition of petroleum varies with locality, but all petroleums usually contain three types of hydrocarbons, viz., paraffins (mainly of normal structure), cycloparaffins (naphthenes), and aromatic hydrocarbons, although the proportions of these hydrocarbons vary, depending on where the petroleum is found.

The petroleum from Mangyshlak is, for example, rich in saturated hydrocarbons, while the petroleum recovered from around Baku contains a lot of cycloparaffins.

In addition to hydrocarbons, petroleum also includes (in smaller quantities) organic compounds containing oxygen, nitrogen, sulphur, and other elements. Petroleum may also contain high-molecular compounds (resins, asphalts). Hundreds of various compounds can be found in petroleum.

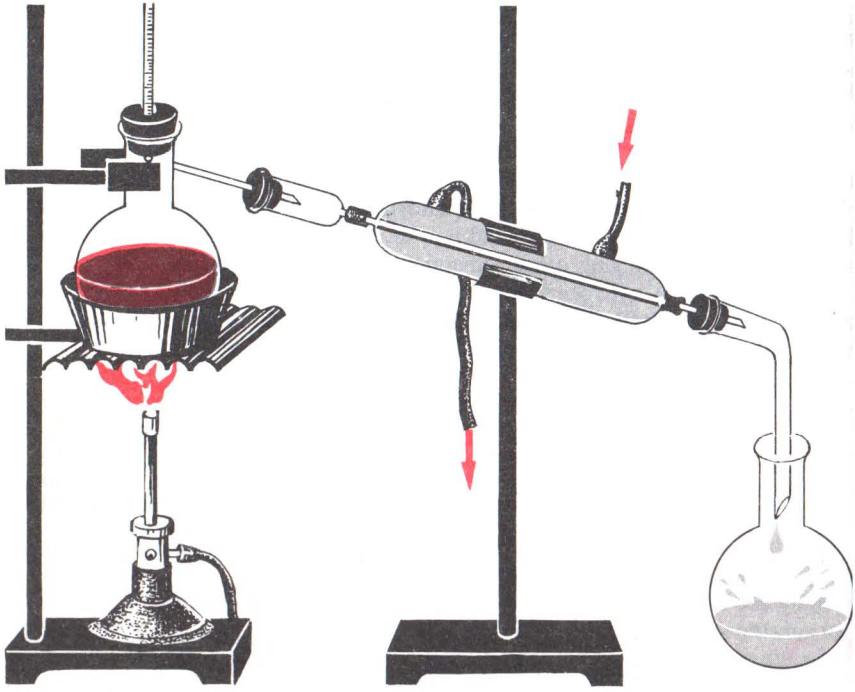


Fig. 29. Petroleum fractionation

Petroleum Products and Their Uses. Since petroleum is a mixture of hydrocarbons with various molecular weights, and boiling at various temperatures, it is distilled into separate fractions, from which the following products are obtained: *petrol*, which contains hydrocarbons with 5 to 11 carbon atoms in their molecules, and is distilled at temperatures from 40 to 200 °C; *ligroin*, containing $C_8$ to $C_{14}$ hydrocarbons, boiling at temperatures from 150 to 250 °C; *kerosine*, which contains $C_{12}$-$C_{18}$ hydrocarbons and boils at 180-300 °C; and *gas oil*. These are the *light petroleum products* (distillates).

Petrol is used as a fuel for lorries, cars, and piston-engine aircraft. It is also used as a solvent for oils and rubber, and as a dry-cleaning agent. Ligroin is used as a fuel for tractor engines. Kerosine is also used as a fuel for tractor engines, and for jet planes and rockets. Gas oil is used as a diesel fuel.

After the light products have been distilled off from petroleum, a black viscous liquid remains. This is called *fuel oil* (*masout*). Masout is further processed to yield lubricating oils.

Petrol can also be recovered from masout (see below). Masout is used as fuel for boilers.

A mixture of solid hydrocarbons, paraffin wax, is obtained from some petroleums. By mixing solid and liquid hydrocarbons, vaseline can be prepared. Some of the uses of paraffin wax and vaseline are already known to you.

Antiknock Properties of Petrols. An important property of petrol, which is used as a fuel for internal combustion engines, is its antiknock properties.

In order to understand the nature of knocking (explosive combustion) in the engine, remember the operation of a car engine. A mixture of petrol vapour and air is sucked into a cylinder, where it is compressed by the piston, and then ignited from a spark plug. As the hydrocarbons burn they produce gas which expands and performs work. The higher the degree to which the gaseous mixture is compressed, the higher the power of the engine, and the lower the consumption of fuel. But not all grades of petrol can stand high compression. Some hydrocarbons ignite prematurely when they are compressed and burn with an explosion. This explosion is heard as a knock in the cylinder. The power of the engine decreases and the engine is soon worn out.

Paraffins of normal structure are the least stable hydrocarbons with respect to detonation. Branched hydrocarbons, and also unsaturated and aromatic hydrocarbons are more stable to detonation and can be compressed to a higher degree, and hence the power of the engine increases.

To characterize the antiknock properties of petrols, each grade of petrol is assigned an *octane number*. An octane number of 0 is given to *n*-heptane, the poorest fuel, while the least detonable fuel, isooctane (2,2,4-trimethylpentane) is given an octane number of 100. Mixtures of heptane and isooctane have octane numbers which show the proportion (in per cent) of isooctane in the mixture. If a petrol is assigned an octane number of 76, this means that it can undergo the same degree of compression as a mixture of 76 per cent isooctane and 24 per cent heptane.

Petrols recovered from petroleum have comparatively low octane numbers, especially if they are rich in paraffins. High-octane petrols are obtained by special methods which shall be discussed later.

1. Can the composition of a petroleum be expressed by a single molecular formula? Explain your answer.
2. Specify (approximately) distillation ranges for petrol, kerosine, and ligroin.
3. What is detonation and what is an octane number?
4. How does the structure of a hydrocarbon account for its antiknock properties?
5. Name the most important petroleum products and what are their uses?

6. Find out which grades of petrol are used in the automobiles at your school or farm. What are their octane numbers?

## 5.3 Petroleum Refining

Let us acquaint ourselves with the methods by which petroleum products are obtained from crude petroleum.

Natural petroleum always contains water, mineral salts, and various solid impurities. Therefore, before petroleum is refined, it must be separated from water, salts, and other undesirable admixtures.

Petroleum Distillation. Petroleum cannot be distilled in industry by the method which we normally use in the laboratory (Fig. 29). The laboratory

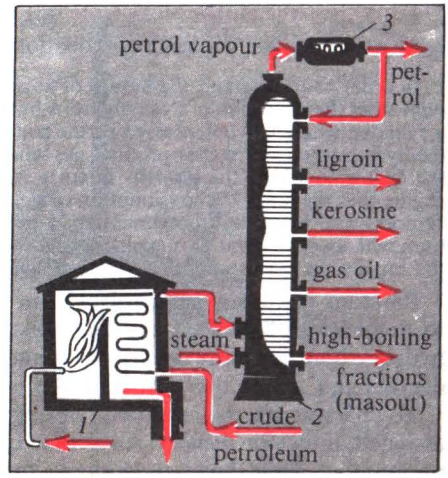



Fig. 30. A continuous fractionating column:

*1*–tube furnace; *2*–fractionating column; *3*–condenser

method is inefficient, much energy is required, and the contents of fractions obtained according to their mol. weight are not precisely defined. Continuous distillation columns (Fig. 30) have none of these disadvantages.

A distillation column consists of a tubular furnace where the petroleum is heated, and a fractionating column, where the petroleum is separated into fractions (distillates) due to their different boiling points.

The furnace has a coil through which the petroleum is passed and heated to 320-350 °C by burning fuel oil or hot gas. A mixture of liquid and vapour is delivered to the fractionating (rectification) column.

The fractionating column is a cylinder made of steel with a height of about 40 metres. It is packed with dozens of horizontal perforated partitions, which are called plates. The petroleum vapour enters the column at the bottom, and rises to the top passing through the perforations in the plates. As the vapour cools down it liquefies, each fraction condensing at its own plate, depending on the range of temperatures within which it boils. Hydrocarbons of less volatile fractions are condensed on lower plates to give the gas oil fraction, more volatile hydrocarbons condense on higher plates to form the kerosine fraction, and still at higher plates the hydrocarbons of the ligroin fraction condense. The most volatile fraction leaves the column as vapour to give petrol. Part of the petrol is returned to the column to irrigate it and to improve the conditions for condensing the rising vapour.

The liquid fraction of the petroleum delivered to the column drips down the plates. This is masout. In order to facilitate the evaporation of volatile hydrocarbons in the masout, superheated steam is fed into the column from the bottom creating a countercurrent flow with the dripping masout.

The separated fractions are withdrawn from the column and purified from other impurities by treating them with sulphuric acid, alkalis, or by other methods. In some petroleum refineries the ligroin and kerosine fractions are not

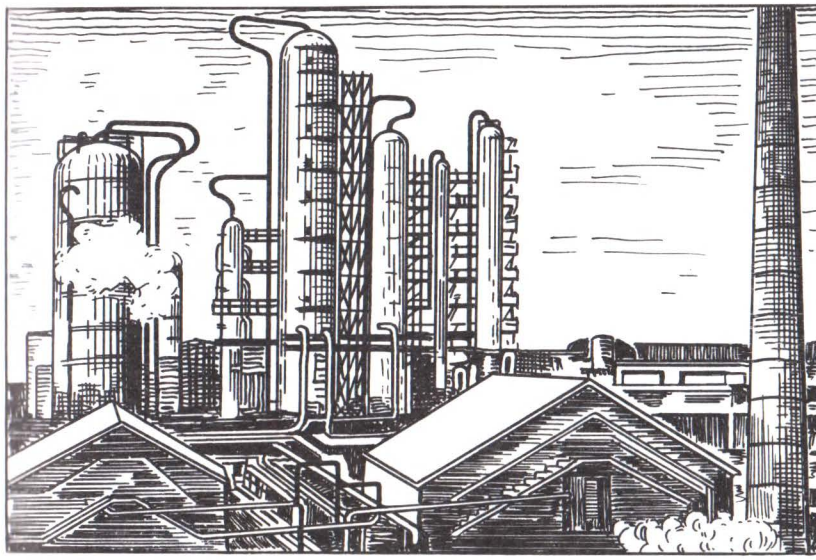


Fig. 31. A general view of the plant for fractionation of crude petroleum. The tube furnace can be seen at the front

separated but are removed from the column as a single ligroin-kerosine fraction, which is used as a jet fuel.

The masout that remains after the fractionation of crude petroleum is a valuable mixture of many heavy hydrocarbons. It is processed into lubricating oils. In order to fractionate the masout, it would have to be heated to temperatures higher than 350 °C (the temperature in the fractionating column). But the hydrocarbons contained in masout cannot stand such high temperatures and would decompose. The process is therefore carried out at low pressures, in vacuum apparatus, and the hydrocarbons of masout are then evaporated at lower temperatures without decomposition.

The vacuum plant looks like a normal distillation column. The masout is first heated in a tube furnace and delivered to the fractionating column. The processes occurring in the column are also about the same as in the previous case: the masout vapours are separated in the column into fractions which condense into various lubricating oils. The bottoms that remain after the separation of the volatile fractions, are *pitch and tars* (road oil).

The fractionation of crude petroleum and masout is now usually performed at plants where processes carried out at atmospheric pressure (distillation of petroleum) and in vacuum (fractionation of masout) are united in a single complex as shown in Fig. 31.

Petroleum Cracking. The amount of petrol that is obtained from the fractionation of crude petroleum cannot meet the increasing demand, and additional sources had therefore to be found. But how could additional

amounts of petrol be produced, if all the light hydrocarbons are extracted from the crude petroleum during fractionation?

We have said that masout cannot be fractionated at atmospheric pressure because its constituents decompose at high temperatures. But this disadvantage can be turned into advantage. Masout can be used as an additional source of petrol. If large molecules of high-boiling hydrocarbons decompose into smaller molecules at high temperatures, then petrol-sized molecules can be obtained. Carry out the following experiment.

Pass kerosine or lubricating oil from a funnel through an iron tube held over a strong flame (Fig. 32). Soon a liquid will collect in the U-tube and gas in the overturned cylinder. This indicates that a chemical reaction has occurred in the tube. The conclusion can be proved by testing the reaction products. Both the liquid and the gas discolour bromine water, while the starting product does not (provided it is sufficiently pure).

The results of the experiment can be explained as follows. The initial liquid hydrocarbon was decomposed by heat, for example

$$\underset{\text{hexadecane}}{C_{16}H_{34}} \rightarrow \underset{\text{octane}}{C_8H_{18}} + \underset{\text{octene}}{C_8H_{16}}$$

to give a mixture of saturated and unsaturated hydrocarbons. The molecular weights of the products are lower than that of the initial hydrocarbon. The mixture obtained is petrol. But it can be further decomposed as follows:

$$C_8H_{18} \rightarrow C_4H_{10} + C_4H_8$$

$$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$$

$$C_4H_{10} \rightarrow C_3H_6 + CH_4$$

These reactions give gaseous substances which are collected in the overturned cylinder.

Hydrocarbons are decomposed at high temperatures with formation of free radicals. Consider this process using pentane as an example. As the hydrocarbon is heated, the chemical bonds weaken, and one of them breaks to form free radicals:

$$CH_3-CH_2-CH_2-CH_2-CH_3 \rightarrow CH_3-CH_2-CH_2^{\bullet} + {}^{\bullet}CH_2-CH$$

Particles with unpaired electrons are known to be short-lived and they are soon stabilized. They can be stabilized by different mechanisms. For example, a double bond can be established if hydrogen atom is split off from a neighbouring carbon atom

$$\underset{\displaystyle H}{CH_2-CH_2^{\bullet}} \rightarrow CH_2=CH_2 + H^{\bullet}$$

In other cases hydrogen atom may combine with a free radical:

$$CH_3—CH_2—CH_2^{\bullet} + H^{\bullet} \rightarrow CH_3—CH_2—CH_3$$

Decomposition of petroleum hydrocarbons into more volatile substances is known as *cracking*. The yield of petrol can thus be increased.

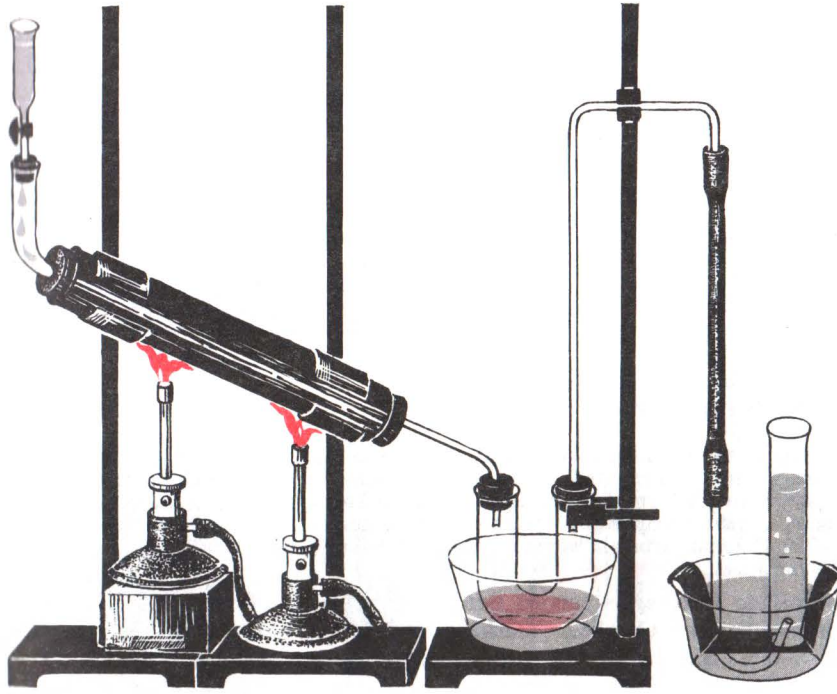


Fig. 32. Kerosine cracking

The industrial cracking process was invented by the Russian engineer Shukhov in 1891.

There are two types of the cracking process: thermal and catalytic. In thermal cracking, the hydrocarbons are broken down at high temperatures, while in the catalytic process the reaction is catalyzed.

*Thermal cracking* in industry is carried out by passing petroleum products, e. g. masout, through a tube furnace, where the initial product is heated to about 470-550 °C under the pressure needed to maintain the hydrocarbons in the liquid state. In these conditions the larger molecules are broken into petrol molecules as described above. In order to separate the formed mixture of liquid and gaseous substances, the cracked products are delivered to the rectification column.

The petrol obtained by thermal cracking differs substantially from the straight-run petrol in that it contains unsaturated hydrocarbons. Since they have higher octane numbers than saturated hydrocarbons, the petrol obtained by cracking has better antiknock properties than the straight-run petrol. But cracked petrol is less stable in storage because its unsaturated hydrocarbons are oxidized and polymerized into resins. The resins clog fuel pipes, produce deposits of carbon on valves and cylinder walls. Antioxidants are added to cracked petrol to make it more stable in storage. The gases produced by thermal cracking are rich in unsaturated hydrocarbons (Fig. 33).

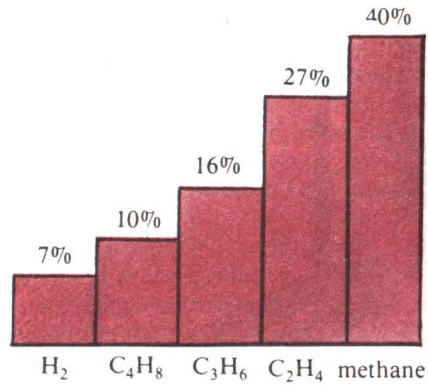



Fig. 33. Tentative composition of a thermally cracked gas

The higher the cracking temperature, the smaller the fragments into which larger molecules are broken, and the greater amounts of gases rich in unsaturated hydrocarbons are formed. High-temperature cracking (*pyrolysis*) is therefore used to obtain gaseous unsaturated hydrocarbons. The process is carried out at a temperature of 650-750 °C. Liquid aromatic compounds (which are valuable products) are also formed with the gases.

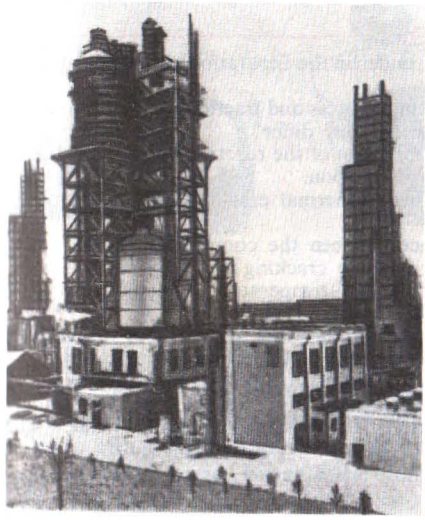
*Catalytic cracking* is carried out in the presence of natural or synthetic aluminosilicates. Catalytic cracking is realized at lower temperatures (450-500 °C) and the process rate is higher. The petrol obtained has a higher quality.

Along with the decomposition reactions, isomerization also occurs during catalytic cracking. The normal hydrocarbons are isomerized into branched hydrocarbons, and the quantity of unsaturated hydrocarbons produced in this process is smaller than that produced in thermal cracking. The quality of the petrol is improved because the presence of branched hydrocarbons increases the octane number of petrol, while the lower unsaturated hydrocarbon content makes the petrol more stable in storage.

The technical realization of catalytic cracking was a complicated problem. The catalyst became quickly contaminated with the nonvolatile products of hydrocarbon decomposition, and thus inactive within a few minutes. The process had to be discontinued and the activity of the catalyst restored by burning out the coke.

The problem seemed to be difficult to solve. But the ingenuity of the investigators saved the situation. Plants were designed in which the catalyst was continually withdrawn from the reactor, its properties recovered in a regenerator, and then the catalyst was returned into the reaction zone. Another solution was the fluidized bed technique. (You should remember this technique as it is used in the manufacture of sulphuric acid.) The operating principle of this process (Fig. 34) is as follows.

The raw material (gas oil) is delivered from a tube furnace and mixed with hot catalyst dust. The evaporated gas oil rises up the reactor in a continuous flow. Since the volume of the reactor is very large, the velocity of the flow drops



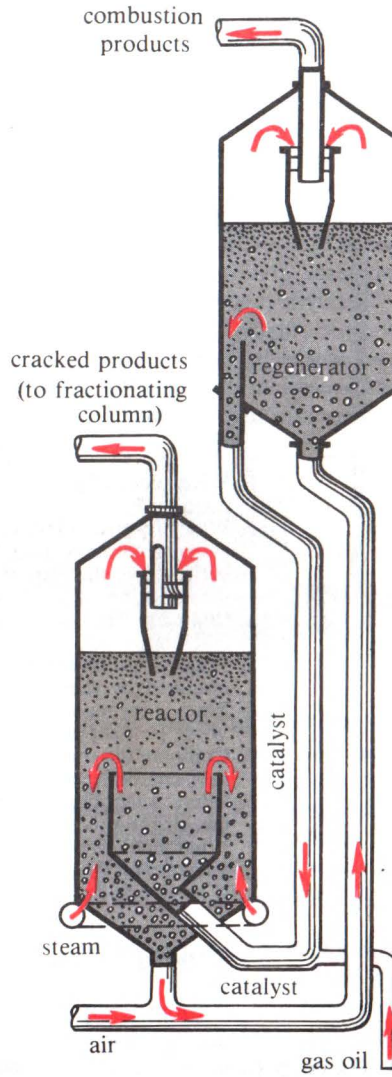



Fig. 34. A plant for catalytic cracking in a fluidized bed

sharply and the catalyst particles form a loose bed in which they are vigorously stirred, like in boiling liquid. The main cracking occurs here.

The cracked products rise to the upper portion of the reaction vessel, pass into a separator, where the catalyst particles precipitate, and then to the rectification column.

The catalyst which has been "coked" by the decomposition products is

continuously withdrawn from the reactor and delivered by an air current into the regenerator. The coke is burned out in the regenerator in the fluidized bed as well. The recovered catalyst is returned to the reactor after having been mixed with the fresh portions of raw materials.

Another important catalytic process used in industry is *aromatization of hydrocarbons*, i. e., the conversion of paraffins and cycloparaffins into aromatic hydrocarbons. Try to remember how hexane and cyclohexane can be converted into benzene.

The aromatization processes also occur during petrol reforming, during which they are heated over a platinum catalyst. The octane number of the petrol increases greatly because of the formation of the aromatic hydrocarbons.

Catalytic methods of petroleum refining are developing rapidly. Many useful organic substances are now obtained by chemical processing of petroleum hydrocarbons. This is done by a special branch of industry known as the petrochemical industry. We shall later discuss the methods by which organic compounds are produced in the petrochemical industry.

? 1. What physical phenomena underlie the separation of petroleum into fractions?

△ 2. Which features do the cracking-process and fractionation of petroleum have in common and how do they differ?

3. Write down the equations for some of the reactions occurring during the cracking of $C_{12}H_{26}$ hydrocarbon.

4. What are the conditions for (a) thermal cracking, and (b) catalytic cracking?

5. What is the main difference between the composition of the gases obtained by thermal and catalytic cracking?

6. What is the main feature of the high-temperature cracking (pyrolysis)? What is the purpose of this process?

7. Compare the composition and antiknocking properties of straight-run and cracked petrols. How can they be distinguished in practice?

8. What scientific principles common to the catalytic cracking of petroleum products and other industrial processes do you know?

9. What does the aromatization of hydrocarbons mean? What is the purpose of this process?

## 5.4 Coking

Another important source of industrial manufacture of aromatic hydrocarbons is coking of coals.

The coking can be carried out in the laboratory (Fig. 35). If a lump of coal is heated strongly in an iron tube in the absence of air, various gases and vapours will soon evolve. A resin with an unpleasant odour, and a supernatant layer of water containing ammonia will collect in the U-tube of the apparatus. The gases that pass through the U-tube are collected in the vessel over water. What remains in the iron tube after the experiment is over, is coke. The collected gas is flammable and is called coke gas.

Four major products are thus obtained by heating coal in the absence of air: *coke, coal tar, ammonia water*, and *coke gas*.

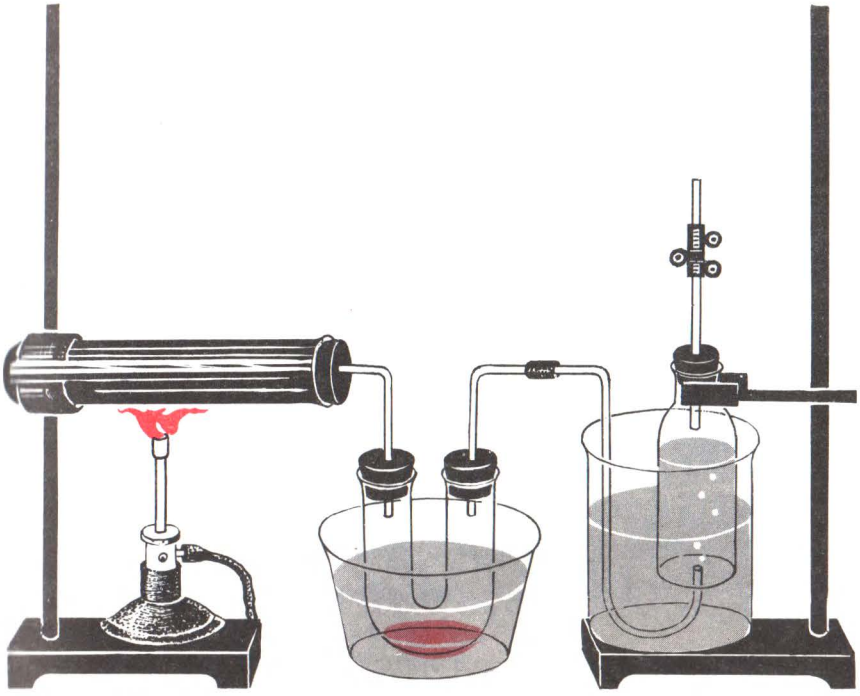


Fig. 35. Coking of coal

Industrial coking has much in common with the experiment that we carried out in the laboratory. What is different is the scale of an industrial plant.

An industrial coke oven (Fig. 36) includes a long narrow chamber into which coal is loaded through the top openings. Blast-furnace gas or coke gas are used to heat the chamber. Several dozen chambers form a battery of coke ovens. In order to attain high temperatures of burning, the gas and air are preheated in regenerators arranged beneath the chambers (like in the open-hearth manufacture of steel).

As the coal is heated to 1 000 °C, the complex organic compounds contained in it undergo chemical conversions to give coke and the volatile products. The coking process continues for about 14 hours. The coke "cake" is discharged from the chamber into ladles and quenched with water or an inert gas. The chamber is loaded with a new charge of coal and the process is repeated. The cooled coke is delivered to blast furnaces.

The volatile products of the coking are withdrawn through the top openings of the chamber into a collecting tank where (just like in our laboratory experiment) resin and ammonia water are condensed.

Ammonia and light aromatic hydrocarbons (mainly benzene) are isolated from the uncondensed gas. In order to extract the ammonia, the gas is passed through sulphuric acid solution, the resultant ammonium sulphate being used as a fertilizer.

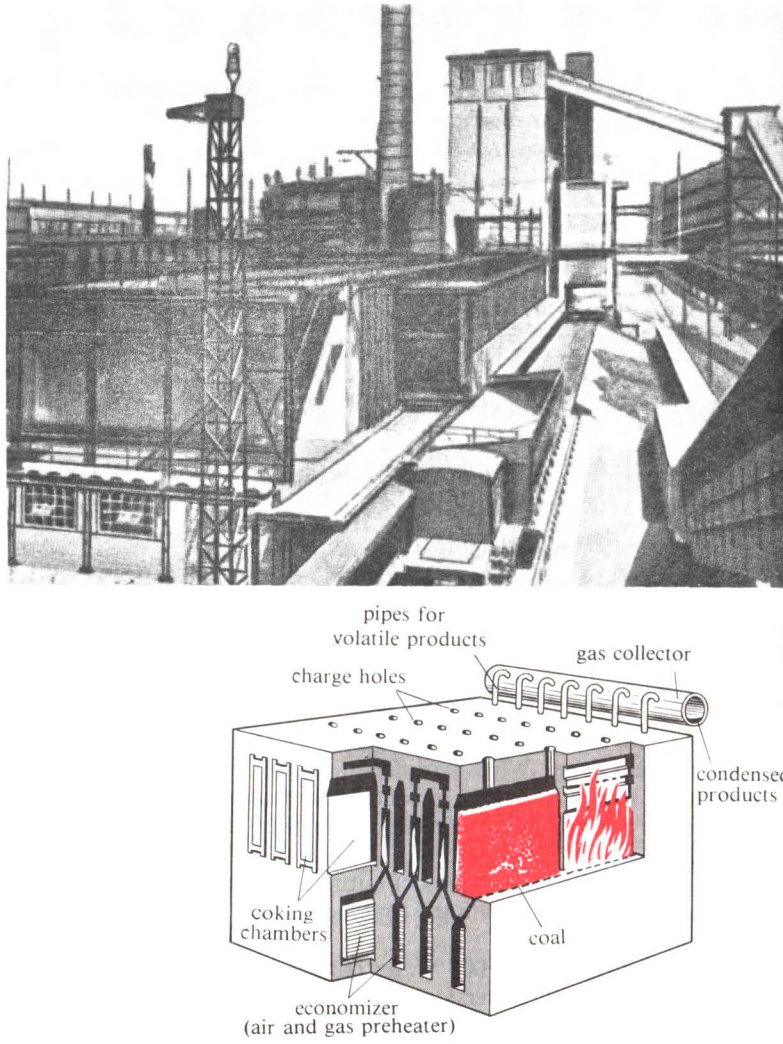



Fig. 36. A battery of coke ovens

Aromatic hydrocarbons are isolated by absorbing them in a suitable solvent and then distilling them from the solution.

Benzene homologues, e.g. phenol (carbolic acid), naphthalene, and many other substances are isolated from coal tar by fractionation.

After purification, coke gas is used as fuel for various processes, such as glass making and open-hearth steel conversion, because it contains many combustible materials (Fig. 37). It is also used as a raw material in the chemical

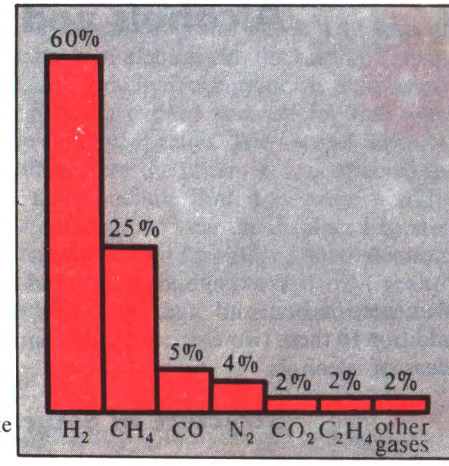



Fig. 37. A tentative composition of coke gas

industry. Hydrogen can be isolated from coke gas and used for the synthesis of various organic products.

The coking process is a batch process, and this has disadvantages, most of which you should be able to list yourself.

Engineers are now working hard to develop a continuous process for coking coal.

1. Once the composition of coke gas is known (Fig. 37), which organic products can be obtained from it?
2. Coke is produced in furnaces by a batch process, but coke gas is processed continuously. Explain why.
3. The ammonia in ammonia water exists both as a dissolved gas and in the form of salts. What method would you suggest for separating as much ammonia as possible from the ammonia water?
4. Why narrow chambers are used for coking coal? If the chambers were wider, they could hold more coal. Explain the paradox.
5. What general scientific principles underlie the coking process?
6. What industrial methods do you know for obtaining aromatic compounds?
7. Generalize your knowledge on the composition and possible uses of (a) natural gas, (b) petroleum gas, (c) gases obtained by thermal and catalytic cracking and by pyrolysis, and (d) coke gas.

# 6 Alcohols and Phenols

We have only studied organic substances formed by two elements, carbon and hydrogen. But there are many substances which, in addition to these two elements, also contain oxygen. First we shall consider the class of alcohols.

## 6.1 Structure of Saturated Monohydric Alcohols

Structure of Ethyl Alcohol. Consider the structure of the compounds belonging to this class using ethyl alcohol as a representative.

Ethyl alcohol, $C_2H_6O$ is a colourless liquid with a specific odour. It is lighter than water (its density being 0.8 g/cm$^3$) and readily soluble in it, boils at 78.3 °C, and dissolves many inorganic and organic substances.

Once we know the molecular formula of alcohol and the valency of the elements composing it, we can try to draw its structure. Two structural formulas are possible:

Which of them is a true structure of ethyl alcohol?

While comparing the formulas we can notice that in one structure all the hydrogen atoms are connected to the carbon atoms, and hence the properties of all hydrogens in the alcohol molecule should be the same. In the other formula, one hydrogen is connected to the carbon atom through the oxygen, and its properties will probably differ from all the other hydrogens in the molecule. It is possible to see experimentally if the properties of all hydrogen atoms in the alcohol molecule are equal.

Place pure alcohol into a dry test tube and add a small piece of sodium metal: liberation of gas begins immediately. It is easy to identify the gas. This is hydrogen. Carry out another, more complicated experiment, to determine the quantity of hydrogen atoms that are liberated by each alcohol molecule during this chemical reaction. Assemble the apparatus shown in Fig. 38. Place some sodium metal into a flask and add a measured quantity of alcohol, e. g. 0.1 mole (4.6 g) from the funnel, drop by drop. The hydrogen evolved displaces water from a two-necked bottle into a measuring cylinder. The volume of the displaced water is the volume of the liberated hydrogen.

The experiment shows that 0.1 mole of alcohol liberates about 1.12 litre of hydrogen (at STP). This means that one mole of alcohol can liberate 11.2 litres (half mole) of hydrogen. In other words, only one hydrogen atom is eliminated from each alcohol molecule. The first formula cannot account for this fact, because all its hydrogen atoms have the same properties. The second formula shows that one of the hydrogen atoms differs from the others: it is connected to the carbon atom through oxygen. We can conclude that it is more weakly attached to carbon, this hydrogen is more mobile and can be displaced by the sodium. The second formula is thus the true structural formula of ethyl alcohol.

In order to indicate that the alcohol molecule contains the hydroxyl group OH, which is bonded to the hydrocarbon radical, the molecular formula of ethyl alcohol is often written as:

$$CH_3—CH_2—OH \text{ or } C_2H_5OH$$

The question arises as to why the properties of the hydrogen atom, that is connected to the carbon through oxygen, are different from those of the other hydrogen atoms in the molecule. The reason is that the atoms in the molecule affect each other. We shall consider the electron structure of the alcohol molecule.

The character of the C—C and C—H bonds is well known to us. These are covalent $\sigma$ bonds. The oxygen atom also establishes the same bonds with the

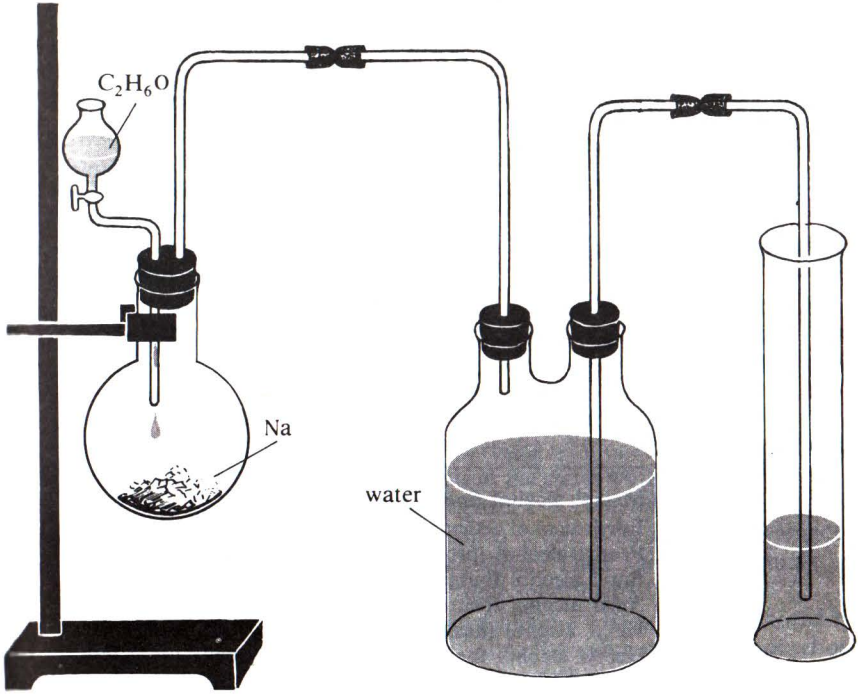
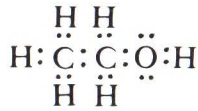
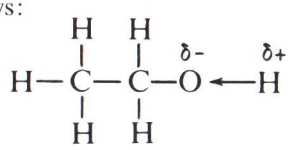



Fig. 38. Determining the quantity of hydrogen liberated from ethyl alcohol

hydrogen atom and the hydrocarbon radical. Its outer electron layer is thus completed to the full octet. The formula of alcohol can be expressed as follows



But the distribution of electron density in the alcohol molecule is not as uniform as in hydrocarbons. The O—H bond is polar because its highest electron density is displaced toward the oxygen atom, which is more electronegative. The hydrogen atom appears to be more free of the electrons, i.e. it is less tightly connected to the molecule, and can therefore be relatively easily displaced by the sodium. The displacement of the electron density can be shown in the formula as follows:



The spatial arrangement of the atoms in the alcohol molecule can be shown by a model (Fig. 39).

The oxygen atom forms covalent bonds with other atoms at a certain angle (not along a straight line). This happens because the outer electron layer of oxygen, in addition to two paired *s* electrons and two paired *p* electrons, also has two unpaired *p* electrons. The axes of these electron clouds are mutually perpendicular. The covalent bonds of the oxygen with the other atoms are formed along these axes. (The valency angle is in fact slightly different from a right angle because of hybridization and some other factors.)

Remember that the molecule of water has a similar spatial structure.

The Alcohol Homologous Series. Ethyl alcohol is a representative of the homologous series of alcohols. Other alcohols have a similar chemical and electron structure. The first member of the series is methyl alcohol

*Table 6.1*

SATURATED MONOHYDRIC ALCOHOLS

| Alcohol | Formula | Boiling point, °C |
|---|---|---|
| Methyl alcohol (methanol) | $CH_3OH$ | 64.7 |
| Ethyl alcohol (ethanol) | $C_2H_5OH$ | 78.3 |
| Propyl alcohol (propanol-1) | $C_3H_7OH$ | 97.2 |
| Butyl alcohol (butanol-1) | $C_4H_9OH$ | 117.7 |
| Amyl alcohol (pentanol-1) | $C_5H_{11}OH$ | 137.8 |
| Hexyl alcohol (hexanol-1) | $C_6H_{13}OH$ | 157.2 |
| Heptyl alcohol (heptanol-1) | $C_7H_{15}OH$ | 176.3 |
| etc. | | |

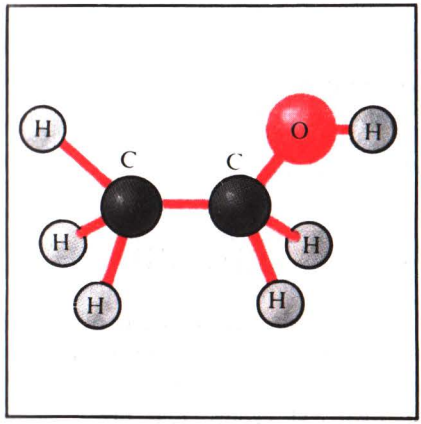
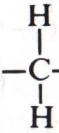
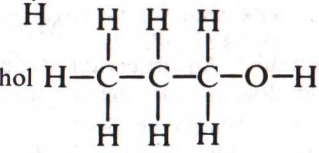



Fig. 39. Models of ethyl alcohol molecule

(methanol):  . The next homologue is ethyl alcohol followed by propyl alcohol  . The homologous series is given in Table 6.1.

Compare the formulas and make sure that the homologous difference in the composition of the molecules is $CH_2$.

A molecule of alcohol may contain not only one, but two or more hydroxyl groups.

It has been shown in the experiment with sodium that the presence of the hydroxyl group in the molecules accounted for the properties of alcohol, i. e. its chemical function. These groups of atoms are called *functional groups.*

●Alcohols are organic substances that contain one or more hydroxyl functional groups attached to the hydrocarbon radical.

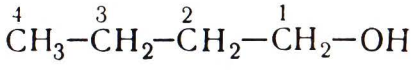
Alcohols can also be regarded as hydrocarbons with one or more hydrogens replaced by the —OH groups. The alcohols in the series we discussed above can be thought of as derivatives of saturated hydrocarbons in whose molecules the hydroxyl group substitutes for one hydrogen atom. This is the homologous series of the *saturated monohydric alcohols.* Their general formula is $C_nH_{2n+1}OH$, or R—OH. Let us first study monohydric alcohols.

The IUPAC name of alcohols containing a single —OH group is obtained by dropping the final *e* and adding the suffix *-ol* to the name of the hydrocarbon. Numbers are used to indicate the carbon atom to which the hydroxyl group is attached (see Table 6.1). The carbon atoms are numbered from the end nearest

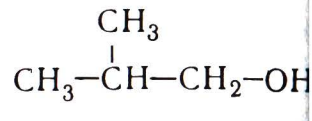
the functional group.

Isomerism of alcohols depends both on the isomerism of the carbon atom chain and the position of the hydroxyl group. We shall consider isomerism in more detail using the butyl alcohols as an example.

Depending on the structure of the carbon chain, two alcohols can be obtained from butane and isobutane

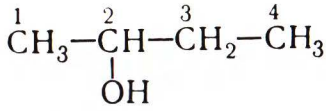


Butanol-1 or
*n*-Butyl alcohol

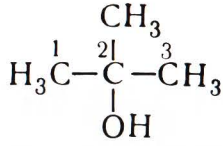


2-Methylpropanol-1 or
isobutyl alcohol

Depending on the position of the hydroxyl group, two other isomeric alcohols are possible:



Butanol-2



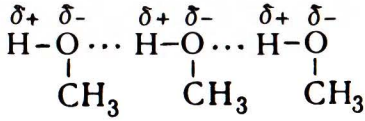
2-Methylpropanol-2

Hydrogen Bonding Between Molecules. An observant student might have already noticed that unlike other homologous series the new homologous series has no gases. The first member of the series, methyl alcohol, is already liquid.

How can this increase in the boiling points of the homologues be explained? Does it depend on the presence of the oxygen atom, which makes the molecule heavier? But the molecular weight of methyl alcohol is 32, while that of propane is 44. Nevertheless, methyl alcohol is a liquid while propane is a gas. The molecular weight of chloromethane is 50.5 and it is a gas as well.

What can then explain the fact that methyl alcohol is a liquid despite its relative lightness?

We have seen that the hydrocarbon radical and the hydrogen atom are not arranged along a straight line but at a certain angle with the oxygen atom in the alcohol molecule. The oxygen atom has free electron pairs and it can therefore interact with a hydrogen atom in another molecule that is slightly positive because of the displacement of the electron density toward the oxygen atom (Fig. 40). This interaction is called hydrogen bonding and is designated in formulas by dots:



The hydrogen bond is much weaker (about ten times) than a normal covalent bond.

Because of the presence of the hydrogen bond, the molecules of alcohol are associated with one another. Additional energy is thus required to break the bonds so that the molecules could be freed from this association and the substance might become volatile. This is why alcohols boil at higher temperatures than the corresponding hydrocarbons.

The formation of hydrogen bonds between the molecules of alcohol and water accounts for the solubility of alcohols in contrast to hydrocarbons, which do not form hydrogen bonds and are therefore insoluble in water. (The C—H bonds of hydrocarbons are very poorly polarized and the positive charge on the hydrogen atoms is too small to form hydrogen bonds.)

The solubility of alcohols in water varies. (Remember that the members of a homologous series differ in some properties.)

Place some water in several beakers, and add equal quantities (e.g. 5 ml) of methyl, ethyl, propyl, butyl, and amyl alcohols. Stir the liquids: the first three alcohols dissolve completely, while butyl and especially amyl alcohol only partially dissolve. The decreasing solubility can be explained by the increasing size of the hydrocarbon radical in their molecules. The larger the radical, the more difficult it is for the hydroxyl group to keep the molecule in solution by the hydrogen bonds (hydrocarbons are insoluble in water).

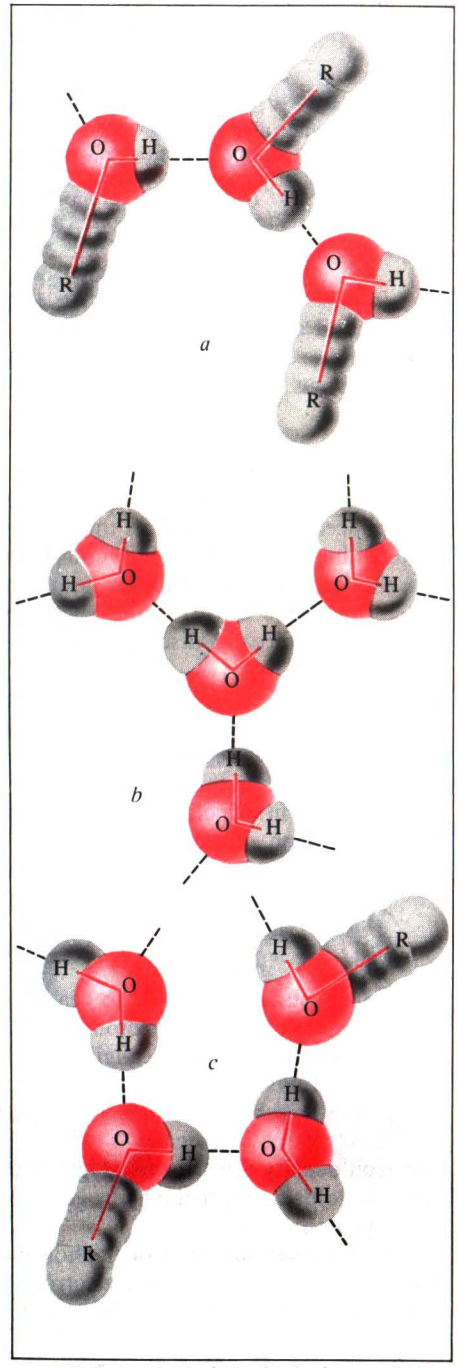



Fig. 40. Formation of hydrogen bonds between molecules:
(a) of alcohol; (b) of water; and (c) of water and alcohol

? 1. Write down the structural formulas for all the isomeric alcohols with the formula $C_5H_{11}OH$.

△ 2. Write down the structural formulas of the following alcohols: (a) 2-methylbutanol-1, (b) 3,3-dimethylpentanol-2.

3. The boiling points of alcohols increase with the number of carbon atoms in their molecule and decrease if there is a branching in the carbon chain. Explain these regularities.

4. The solubility of monohydric alcohols decreases with increasing their molecular weight. Explain why.

## 6.2 Chemical Properties and Uses of Some Monohydric Alcohols

Chemical Properties. Being substances rich in carbon and hydrogen, alcohols burn when lit to liberate heat:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + 1374\ kJ$$

But the mode of burning varies with alcohols.

Place 1 ml portions of various alcohols in porcelain dishes and light them. It can be seen that the alcohols that come first in the series ignite easily and burn with a bluish, almost non-luminous flame, while alcohols with higher molecular weights burn with a luminous flame and leave dark deposits on the porcelain after they have burnt to the end. Explain this phenomenon.

We have already discussed the reaction of ethyl alcohol with sodium:

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$$

The product of sodium substitution for the hydrogen in ethyl alcohol is *sodium ethylate* and can be isolated as a solid. Other soluble alcohols react with the alkali metals in the same way to give *alcoholates*. Write down an equation of the reaction in which sodium propylate is formed.

The reaction of alcohols with metals goes via ionic splitting of the polar O—H bond and can be expressed as follows:

$$2C_2H_5\overset{\delta-}{O}:\!\overset{\delta+}{H} + 2Na \longrightarrow H_2 + 2Na^+ + 2\left[C_2H_5O:\right]^-$$

(the $2\bar{e}$ electron pair moves from the O—H bond to the oxygen atom)

We can state that in these reactions, alcohols have acid properties and eliminate hydrogen as a proton. But alcohols are not considered to be acids, because they dissociate negligibly. They actually dissociate less than water. Their solutions do not change the colour of indicators.

The lower dissociation of alcohols (compared with water) can be explained by the effect of the hydrocarbon radical: the displacement by the radical of the electron density toward the oxygen atom increases its negative charge so that oxygen holds stronger the hydrogen atom, and the elimination of the hydrogen as a proton is difficult.

The dissociation degree of alcohols increases if a substitute is introduced into its molecule that attracts the electrons of the chemical bond. The dissociation degree of 2-chloroethanol $ClCH_2—CH_2OH$ is several times higher than that of

ethyl alcohol. This can be represented as follows:

$$Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow O \leftarrow H$$

The chlorine atom attracts the electron density of the Cl—C bond, and the carbon atom acquires a partial positive charge. In order to compensate for the charge, the carbon atom attracts the electron density of the C—C bond. The electron density of C—O bond is displaced slightly to the carbon atom and the electron density of the O—H bond is displaced from the hydrogen to the oxygen atom. The probability of splitting off hydrogen in the form of the proton increases and the dissociation degree increases too.

Not only the hydroxyl hydrogen but also the whole hydroxyl group can participate in chemical reactions. If ethyl alcohol is heated with a hydrohalic acid (e.g. hydrobromic acid)* in a flask connected to a condenser as shown in Fig. 41, it will be seen that a heavy liquid is collected under the water in the receptacle. This is ethyl bromide:

$$C_2H_5\boxed{OH+H}Br \longrightarrow C_2H_5Br+H_2O$$

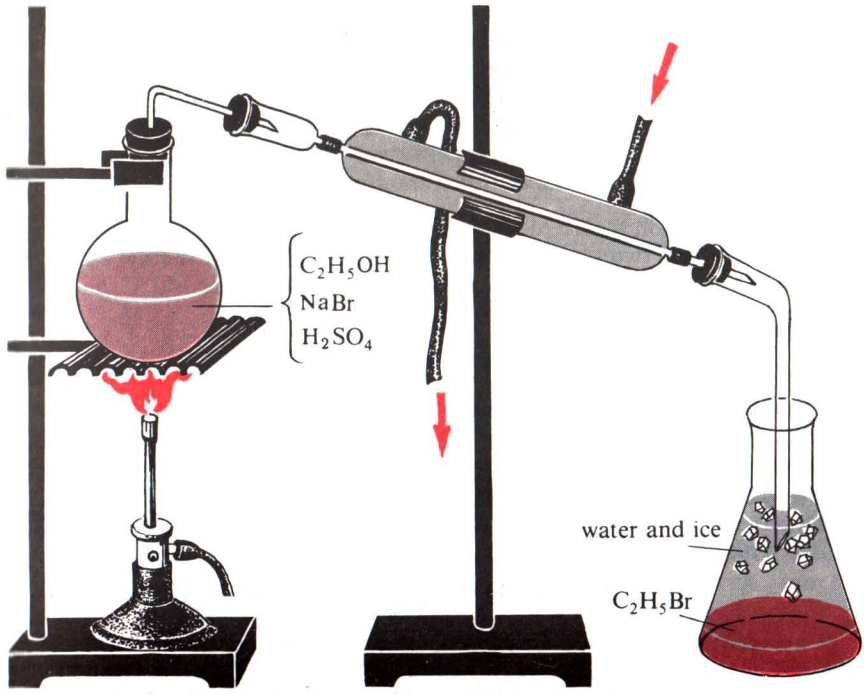



Fig. 41. Preparing ethyl bromide from ethyl alcohol

* Hydrogen bromide can be prepared by the reaction of potassium bromide or sodium bromide with sulphuric acid.

This reaction proceeds with the ionic splitting of the covalent C—O bond. This can be written as follows:

$$C_2H_5\overset{\delta+}{\}}:\overset{\delta-}{O}H + H\overset{\delta+}{\{}:\overset{\delta-}{Br} \longrightarrow C_2H_5Br + H_2O$$

Bases react in a similar way. Methyl bromide can be prepared from methyl alcohol in the same way:

$$CH_3[OH+H]Br \longrightarrow CH_3Br + H_2O$$

When heated in the presence of concentrated sulphuric acid (catalyst) alcohols are easily dehydrated, that is they lose a molecule of water. Ethyl alcohol, for example, yields ethylene

$$\begin{array}{l} H\ \ H \\ |\ \ | \\ H-C-C-H \\ |\ \ | \\ [H\ \ OH] \end{array} \longrightarrow CH_2=CH_2 + H_2O$$

Dehydration of other homologues gives the other unsaturated hydrocarbons:

$$\begin{array}{l} H\ \ H\ \ H \\ |\ \ |\ \ | \\ H-C-C-C-H \\ |\ \ \ \ | \\ H\ \ [H\ \ OH] \end{array} \longrightarrow CH_3-CH=CH_2 + H_2O$$

Propylene

If the dehydration is carried out in different conditions, a molecule of water can be taken from two (not from one) molecules of alcohol. If ethyl alcohol is heated only slightly in the presence of sulphuric acid (under 140 °C, and ethyl alcohol being taken in excess), diethyl ether is formed:

$$C_2H_5O[H + HO]C_2H_5 \longrightarrow C_2H_5 - O - C_2H_5 + H_2O$$

Diethyl ether (or simply ethyl ether) is a volatile, easily flammable liquid. It is used as a solvent and for anaesthesia in medicine (hence, another name for it is anaesthesia ether). It belongs to the class of organic compounds whose molecules consist of two hydrocarbon radicals connected via an oxygen atom. These are *ethers*. The general formula for ethers is R—O—R.

Other ethers are obtained by the dehydration of ethyl alcohol homologues:

$$CH_3O[H + HO]CH_3 \rightarrow CH_3-O-CH_3 + H_2O$$

If a mixture of alcohols is dehydrated, ethers with non-symmetric structures are produced:

$$CH_3O[H + HO]C_2H_5 \rightarrow CH_3-O-C_2H_5 + H_2O$$

Other ethers can also be formed by this reaction; name them and write down the reaction equations.

We have never used the name dimethyl ether in this textbook, but you already know its structural formula. Do you remember our discussion of the

possible structural formula of ethyl alcohol? Of the two possible structural formulas expressed by one molecular formula $C_2H_6O$ we chose the second one because it explained the properties of alcohol. The other formula, which we rejected, was the formula for dimethyl (methyl) ether. Since they have the same molecular formula, ethyl alcohol and methyl ether are isomers, although they belong to different classes of organic compounds. In fact all the saturated monohydric alcohols are isomers of ethers having the same number of carbon atoms in their molecule. What ether is, in your opinion, an isomer of propanol?

Special care should be taken when handling alcohols. Methyl alcohol is very poisonous and even a small quantity of this alcohol can cause blindness and death.

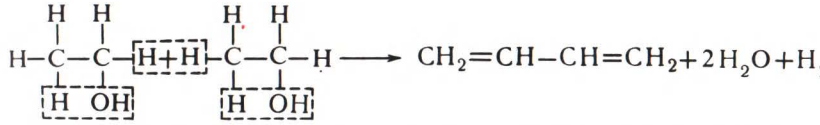
Ethyl alcohol is a narcotic. It is quickly absorbed by the blood making the person excited. A habitual intake of ethanol has a grave effect on the nervous system, alimentary tract, and the cardiovascular system. Ethyl alcohol poisoning can also lead to death. To stop people drinking ethanol intended for industrial use, it is mixed with compounds that taste awful and are possibly poisonous. It is easy to distinguish this sort of alcohol (called denatured alcohol) by its colour and objectionable odour.

Uses of Alcohols. Alcohols are used in many industries as solvents. In the chemical industry they are used for organic syntheses.

Large quantities of methyl alcohol are used for making formaldehyde, which is a raw material for the production of plastics and some other organic substances. At the present time, investigators are working hard to develop new processes by which methyl alcohol can be converted into other products. Hence the increasing importance of methyl alcohol.

Ethyl alcohol is widely used everywhere. Its large quantities are required for making butadiene (for the synthesis of rubber).

Butadiene is made by dehydrogenation and dehydration of ethyl alcohol. These reactions occur simultaneously as the alcohol vapour is passed over a mixture of certain catalysts:




Ethyl alcohol is oxidized to give acetic acid (vinegar). Diethyl ether is obtained by dehydration of ethyl alcohol. Ethanol reacts with hydrogen chloride to yield ethyl chloride which is used in medicine as a local anaesthesia. Alcohol is used in the manufacture of many medicines and cosmetics (perfumes, etc.). Its high heat of combustion and antiknock properties account for its use as a fuel for internal combustion engines (in a mixture with benzene).

? 1. How much methyl alcohol (in grams) has to be burnt to obtain 56 litres of carbon dioxide (at STP)?

△ 2. What volume of air (at STP) is required to burn 23 g of ethyl alcohol? How many moles of carbon dioxide and water are produced in this reaction?

3. How can the acidic properties of the alcohols be explained?

4. What is the maximum volume of hydrogen (at STP) that can be displaced by sodium from 230 g of ethyl alcohol?

5. With which metal will, in your opinion, the alcohols react more energetically than with sodium? Write down the ionic equation for the

reaction.

6. The dissociation degree of 2,2-dichloroethanol, $Cl_2CH—CH_2OH$, is higher than that of 2-chloroethanol $ClCH_2—CH_2OH$. Explain.
7. As hydrogen chloride is passed through methyl alcohol, the chlorine derivative of methane is formed. Write down the reaction equation and name this substance.
8. How can ethyl chloride be obtained from ethyl alcohol? By what other reaction can this substance be prepared? Give the reaction equations.
9. Write the equations for the formation of (a) 1-bromopropane from the corresponding alcohol, and (b) sodium methylate. Indicate the ionic mechanism of the reactions.
10. As a mixture of ethyl and propyl alcohol is heated with concentrated sulphuric acid, a mixed ethylpropyl ether is produced. Write down the reaction equation. What other ethers can be formed in this reaction?
11. How can propanol-1 be converted into propanol-2?

## 6.3 Alcohols as Substituted Hydrocarbons. Industrial Synthesis of Ethanol

**Ties Between Alcohols and Hydrocarbons.** We have seen above that alcohols can be regarded as the hydroxyl substituted hydrocarbons. They can also be regarded as partly oxidized hydrocarbons because in addition to hydrogen and carbon, they also contain oxygen.

It is difficult to substitute the hydroxyl group for the hydrogen atom directly or to attach oxygen to the hydrocarbon molecule. This can be easier done through their halogen derivatives.

For example, in order to obtain ethyl alcohol from ethane, ethyl bromide may be first prepared:

$$C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$$

and the ethyl bromide can then be converted into the alcohol by heating it with water in the presence of an alkali

$$C_2H_5\boxed{Br + H}OH \rightleftarrows C_2H_5OH + HBr$$

The alkali is necessary to neutralize the hydrogen bromide and to stop it reacting with alcohol, i.e. to shift the chemical equilibrium in the direction of formation of the product desired.

Methyl alcohol can be obtained from methane in the same way:

$$CH_4 \rightarrow CH_3Br \rightarrow CH_3OH$$

This method has no industrial importance and is only used in the laboratory. But it has a theoretical importance because it demonstrates the ties between saturated hydrocarbons, the halogen substituted hydrocarbons, and alcohols.

Alcohols are also related to unsaturated hydrocarbons. Since unsaturated hydrocarbons are readily available for modern organic synthesis, they are often used in industry for the manufacture of alcohols. We shall consider the manufacture of ethanol in more detail.

**Industrial Synthesis of Ethanol.** Ethyl alcohol can be prepared in industry by different methods.

The traditional method consists in distillation of ethyl alcohol from wine, where it is formed by the fermentation of simple sugars (grape sugar). Later the method of yeast

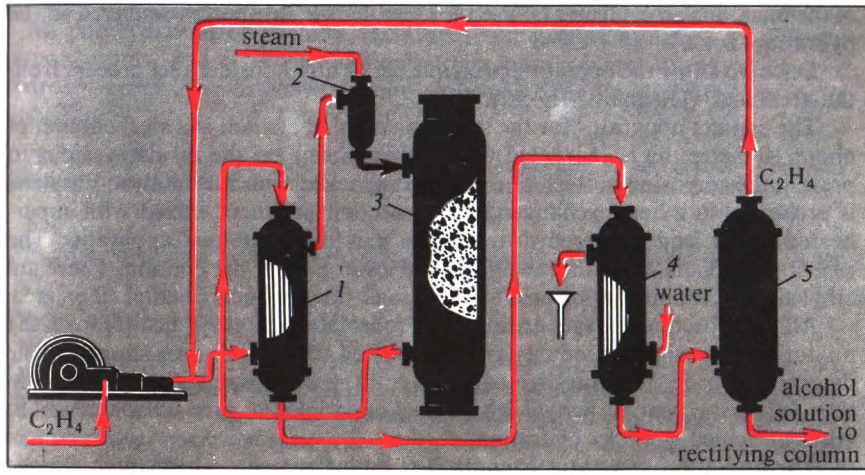



Fig. 42. An industrial plant for direct hydration of ethylene:
*1* heat exchanger; *2*–mixer; *3*–synthesis column; *4*–condenser; *5*–gas separator

fermentation was introduced into industry, in which the ethyl alcohol was produced from starch. Potato or grain starch was first converted into the sugar (maltose), which is then fermented by the yeast into alcohol. Yeast fungi produce a special substance (enzyme) which catalyzes the fermentation process. However, valuable materials that could otherwise be used as food are wasted in the manufacture of alcohol by this method.

At the present time ethyl alcohol is mostly produced from cellulose (wood). Like starch, the cellulose is first converted into a sugar (glucose), which is then fermented into alcohol.

But the most efficient method of producing alcohol is organic synthesis. It consists in catalytic hydration of ethylene with steam. We already know that this reaction is reversible; it is expressed by the equation

$$C_2H_4 + H_2O \rightleftarrows C_2H_5OH + 46\ kJ$$

Since the ethylene and water react in the gaseous state (vapours) and the reaction in this direction proceeds with the reduction of the number of molecules in the mixture, increased pressure shifts the equilibrium towards the formation of ethyl alcohol. In order to ensure a high reaction rate, the reactants should be heated over a suitable catalyst. Since the reaction is exothermic, the excess heat will accelerate the reaction which occurs with absorption of heat, i. e. the alcohol formed will decompose and the equilibrium will be shifted in the reverse direction.

It has been established that the optimum conditions for the hydration of ethylene are a temperature of 280–300 °C and a pressure of 7–8 MPa; the most suitable catalyst is phosphoric acid precipitated on a solid carrier.

As ethylene passes through a contact apparatus, about 5 per cent of its initial quantity is converted into alcohol. In order to raise the efficiency of the process, the alcohol should be separated from the reaction products and the remaining ethylene should be recycled for additional hydration. The products

of the reaction can evidently be used for heating the substances delivered to the hydration zone.

Once we know the operating principle, let us now consider this process from the technical viewpoint (Fig. 42).

The contact apparatus for the synthesis of ethyl alcohol is a steel column of about 10 metres high. It is lined with copper sheets on the inside in order to prevent the corrosion of steel. The column is packed with the catalyst. Ethylene is preheated in a heat-exchanger by the reaction products, mixed with superheated steam, and delivered to the upper part of the contact apparatus. The reaction products are withdrawn from the lower part of the column. These are ethyl alcohol vapours, unreacted ethylene, and side products (diethyl ether, etc.).

All the subsequent stages are intended to isolate pure ethyl alcohol from the mixture. The reaction products are first treated with alkali (not shown in the diagram) in order to neutralize partially entrapped phosphoric acid. They are then fed to the heat exchanger where they are cooled to give off their heat to ethylene which goes to hydration.

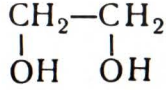
The hydration apparatus is controlled by instruments which maintain the required temperature, pressure of ethylene at the entrance to the reactor and at its exit, the flow rate of the circulating gas and steam, and many other parameters of the process.

? △

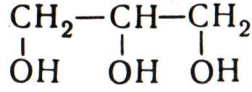
1. Write down the equations for the reactions by which (a) methanol can be obtained from methane, and (b) butanol-1 from butane.
2. Describe two methods by which ethanol can be obtained from ethene.
3. How can propane be obtained from propanol? Write down the reaction equations.
4. Propanol-2 is obtained industrially by the hydration of propene. Is this in agreement with the Markownikoff rule? Use the electron theory to explain your answer.
5. Specify the optimum conditions for the industrial hydration of ethylene and substantiate your answer.
6. What general scientific principles underlie the chemical processes of the hydration of ethylene into ethyl alcohol?

## 6.4 Polyhydric Alcohols

Structure and Physical Properties. Polyhydric alcohols contain several hydroxyl groups connected to the hydrocarbon radicals. The alcohols may be *dihydric*, *trihydric*, etc., according to the number of hydroxyl groups they contain. The simplest representative of dihydric alcohols is ethylene glycol:

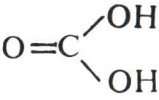


The simplest trihydric alcohol is glycerol (glycerin)



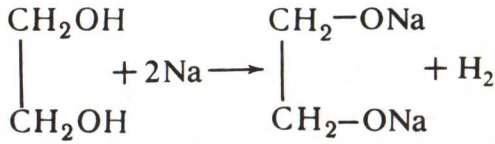
Polyhydric alcohols may contain many hydroxyl groups in their molecules.

All polyhydric alcohols have their hydroxyl groups attached to different carbon atoms, and it is very difficult to prepare an alcohol in which two hydroxyl groups are attached to one carbon atom: the compound is quite unstable.

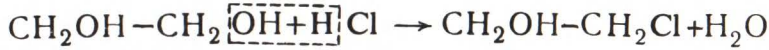
The instability of compounds with two hydroxyl groups at one carbon atom was already discussed in the course of inorganic chemistry, when we studied carbonic acid. This acid, its structural formula is  can only exist in solution. When isolated it decomposes into carbon dioxide and water.

The important polyhydric alcohols, ethylene glycol and glycerol, are colourless syrupy liquids, sweetish to taste, and readily soluble in water.

Chemical Properties. Being substances with hydroxyl groups, polyhydric alcohols have common properties with monohydric alcohols. Sodium, for example, can displace hydrogen from them



In the reaction between hydrohalic acids and alcohols, the hydroxyl group is replaced by the halogen:



But polyhydric alcohols have their own properties. Place some potassium or sodium hydroxide solution into a test tube and add a few drops of blue vitriol (copper sulphate) solution: copper hydroxide $Cu(OH)_2$ is formed. Now add glycerol to the obtained $Cu(OH)_2$. A clear bright blue solution of copper glycerate is formed. (Its structure is very complicated and is not therefore given in this textbook.)

The formation of bright blue solution by the interaction with cupric hydroxide is characteristic of polyhydric alcohols.

Using polyhydric alcohols as an example, we can have another proof of the transition of quantity to quality: the increasing number of hydroxyl groups in a molecule accounts for the appearance in alcohols of new properties compared with monohydric alcohols.

Obtaining Polyhydric Alcohols and Their Uses. Like monohydric alcohols, polyhydric alcohols can be obtained from the corresponding hydrocarbons through their halogen derivatives.

Glycerol, the most widely used polyhydric alcohol, is obtained by splitting fats (try to remember the composition of fats from your general biology course). At the present time glycerol is also synthesized from propylene, which is formed during cracking of petroleum.

Ethylene glycol is used in the manufacture of some organic compounds, e. g.

synthetic fibres, and in large quantities in the manufacture of antifreezes (fluids used in automobiles).

During winter, when the temperature drops below zero, the water used to cool the engine can freeze thus causing a serious damage to the cooling system and the engine. If enough ethylene glycol is dissolved in the cooling water, the freezing point of the solution decreases significantly. A solution containing 25 per cent of ethylene glycol will freeze at $-12\,^{\circ}C$, while solutions containing 55 per cent of ethylene glycol freeze only at $-40\,^{\circ}C$.

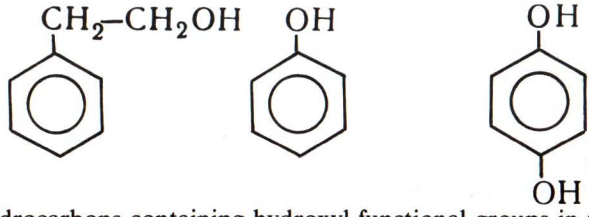
Many of the uses of glycerol depend on its hygroscopic properties. Glycerol is used in medicine to soften the skin and prepare ointments; in leather industry it is used to treat leather to prevent it from drying, and in textile industry, to treat fabrics in order to make them soft and elastic. Glycerol is used to prepare synthetic resins and explosives (e.g. nitroglycerin).

1. Can the tetrahydric alcohol erythritol ($CH_2OH—CHOH—CHOH—CH_2OH$) be regarded as a homologue of glycerol? Explain your answer.
2. Write the structural formulas of the nearest homologues of (a) ethylene glycol, (b) glycerol.
3. Explain the following: ethylene glycol and glycerol (a) are liquids, (b) have comparatively high boiling points, (c) are readily soluble substances.
4. How can glycerol be obtained from 1,2,3-trichloropropane $CH_2Cl—CHCl—CH_2Cl$? Write the equation for the reaction and specify the conditions under which it can be realized.
5. What is the maximum volume of hydrogen (at STP) that can be obtained from one mole of glycerol by reacting it with sodium?
6. How can glycerol be distinguished chemically from ethyl alcohol?

■ 7. Find out if antifreeze is used in cars in your locality. Discover the composition of antifreeze and how it should be used.

## 6.5 Phenols

Aromatic Alcohols and Phenols. Like hydrocarbons with an open chain, aromatic hydrocarbons also have hydroxyl derivatives. The hydroxyl groups may be attached to the carbon atoms of the side chains or directly to the carbon atoms of the benzene ring, e.g.:

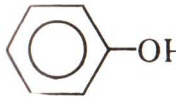



Aromatic hydrocarbons containing hydroxyl functional groups in their side chains are called aromatic alcohols.

Aromatic alcohols are similar to ordinary alcohols in their properties and we shall not discuss them here.

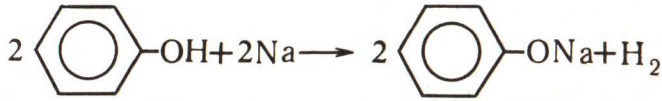
Aromatic hydrocarbons, which contain hydroxyl functional groups in their

*benzene rings*, are called *phenols* (as distinct from alcohols).

The simplest phenol is the monohydric substituted benzene $C_6H_5OH$ or  , and is known as phenol, or carbolic acid. A model of the phenol molecule is shown in Appendix in Fig. III.

Properties of Phenol. Phenol is a white crystalline substance with a characteristic odour. It can turn pink if partially oxidized in air. Phenol has a low melting point, and this can easily be shown if a sample of phenol is kept in a test tube in hot water: the phenol quickly melts (m.p. 42 °C).

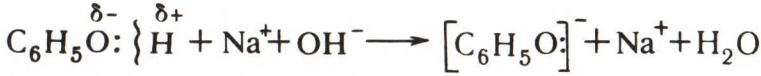
The presence of the hydroxyl group connected to the hydrocarbon radical, accounts for phenol's chemical similarity to monohydric alcohols. For example, if a grain of sodium is added to molten (slightly heated) phenol, hydrogen is liberated, like in reactions with alcohols. Sodium phenolate $C_6H_5ONa$ is formed by this reaction



As distinct from the alcoholates, a phenolate is formed also by the action of an alkali on phenol. The solid soon disappears because sodium phenolate is a readily soluble substance:

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

The ionic equation of this reaction is as follows:



In these reactions phenol acts like an acid. The dissociation degree of phenol is higher than that of water or saturated alcohols. That is why it is also called carbolic acid. But phenol is a weak acid: even carbonic acid is stronger, because it can displace phenol from sodium phenolate.

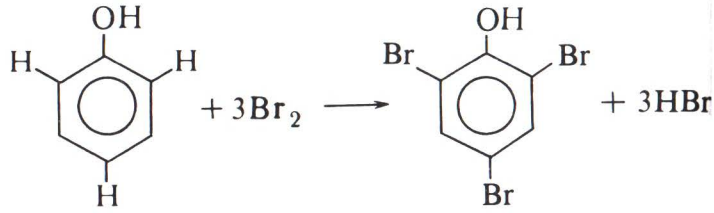
Why do acidic properties increase in phenol? In other words, why can a proton be eliminated from phenol more easily than it can from ordinary monohydric alcohols? These substances differ only in terms of their hydrocarbon radicals. Therefore, unlike the ethyl radical $—C_2H_5$, the phenyl radical $—C_6H_5$ affects the hydroxyl group to weaken its hydrogen-to-oxygen bond.

This is because the benzene ring attracts the electrons of the hydroxyl's oxygen atom to displace the electron density of the O—H bond away from the hydrogen towards the oxygen. The bond becomes more polar and so the probability that the hydrogen can be eliminated as a proton increases.

Let us now consider the behaviour of the hydrogen atoms of the benzene ring in this compound. Are their properties the same as in benzene?

Remember that benzene does not react with bromine water. If bromine water

is added to phenol solution, white tribromophenol precipitates:




The higher reactivity of the benzene ring is explained by the presence of the hydroxyl group in its molecule, since the structures of phenol and benzene are otherwise the same. The electrons of the oxygen atom are attracted to the benzene ring and thus increase the electron density in it, especially at positions 2, 4 and 6, like in the case with toluene. The bromine attacks at these positions.

Here the mutual effect of atoms in the molecule is illustrated once again. Not only does the benzene ring affect the hydroxyl group in the phenol molecule (to increase its acidic properties), but the hydroxyl group also affects the benzene ring to facilitate hydrogen substitution in it.

Uses of Phenol. Its Preparation. Phenol kills many microorganisms and has therefore long been used (in the form of an aqueous solution) to disinfect surgical instruments, furniture, rooms, etc. It is also used in the manufacture of dyes and medicines. Large amounts of phenol are used for making phenol-formaldehyde resins, substances currently used everywhere.

Phenol for industrial uses is mainly obtained from coal tar. But this process, however, cannot satisfy the growing demands for phenol. Large amounts of phenol are now synthesized from benzene.

A very important problem requiring thoughtful consideration when manufacturing phenol is environmental protection. Industrial wastes containing phenol are a great hazard to the animal and plant world. Various methods are used to prevent contamination of the environment with phenol. Gases containing phenol are oxidized catalytically, effluents are treated with ozone, phenol is extracted by solvents, etc. Scientists continue to search for other effective means to protect the environment from phenol.

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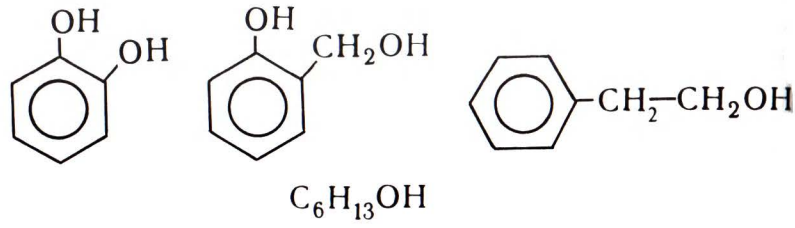
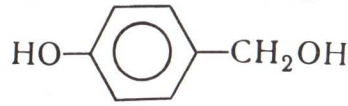
? △ 1. Consider the formulas below and decide to what classes these compounds belong:



2. A substance has the following structure:




How will it react with (a) sodium, (b) sodium hydroxide? Write down the equations for the reactions.

3. The crystalline state of phenol depends on hydrogen bonds between its molecules. How strong are these bonds in comparison with the hydrogen bonds uniting the molecules of monohydric alcohols? Draw a scheme showing the hydrogen bonds in phenol.
4. Why does an aqueous solution of sodium phenolate turn cloudy if carbon dioxide is passed through it? Write down the reaction equation.
5. Phenol readily reacts with nitric acid to give 2,4,6-trinitrophenol (picric acid). Write down the reaction equation.
6. Phenol can be prepared by a chain of the following conversions: $C_6H_6 \rightarrow C_6H_5Cl \rightarrow C_6H_5OH$.
Suggest a method for realizing each of these conversions. Write down the equations for the reactions.

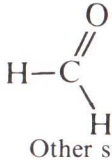
# 7 Aldehydes and Carboxylic Acids

Alcohols are substances obtained by the oxidation of hydrocarbons. Aldehydes and carboxylic acids are products of the oxidation of alcohols.

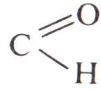
## 7.1 Aldehydes

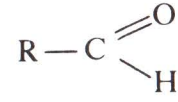
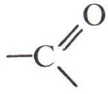
Structure and Physical Properties. In order to understand the structure of aldehydes, consider their simplest representative, formic aldehyde (formaldehyde).

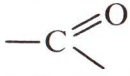
The study of the composition of formaldehyde shows that its molecular formula is $CH_2O$. The only possible structural formula of formaldehyde is

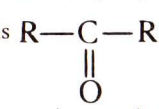


Other substances of this series have a similar structure. The simplest aldehydes are given in Table 7.1.

●Aldehydes are organic substances whose molecules contain the functional group  connected to the hydrocarbon radical*.

The general formula of the aldehydes is  and the  group is called carbonyl. Models of aldehydes are given in Fig. 43 and Fig. IV (see Appendix).

Aldehydes can also be considered as organic compounds whose carbonyl group  *is connected to the hydrocarbon radical and to the hydrogen atom.* Aldehydes differ from ketones in that the carbonyl group in ketones *is connected to two hydrocarbon radicals.*

The general formula of ketones is  . The most important representative

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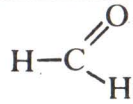
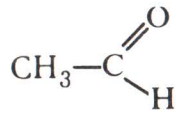
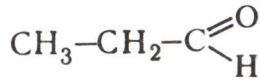
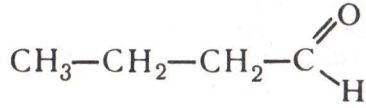
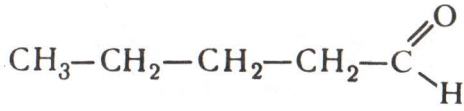
* The functional group is attached to the hydrogen atom in formaldehyde.

HOMOLOGOUS SERIES OF ALDEHYDES

| Aldehyde | Formula | B. p., °C |
|---|---|---|
| Formic aldehyde (formaldehyde) |  | − 19 |
| Acetic aldehyde (acetaldehyde) |  | + 21 |
| Propionic aldehyde |  | + 50 |
| Butyric aldehyde |  | + 75 |
| Valeric aldehyde |  | + 120 |

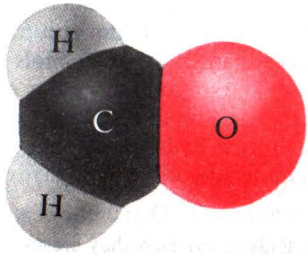



Fig. 43. A model of a formaldehyde molecule

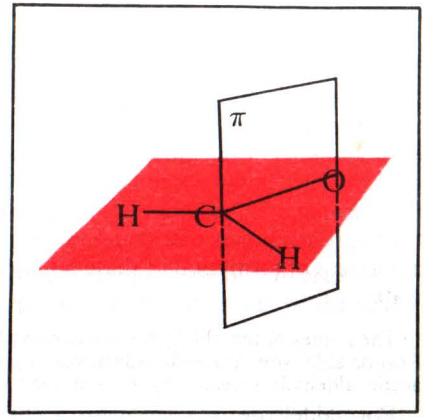
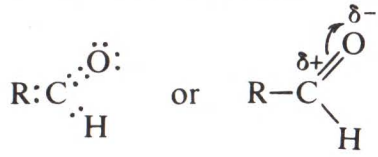



Fig. 44. Formation of the π bond in the carbonyl group of aldehydes

of ketones is *acetone* $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$. This is a colourless liquid with a specific odour. Acetone is widely used as a solvent in industry and in the home.

Let us consider the electron structure of aldehydes. The carbon of the carbonyl group is connected to three other atoms via σ bonds. As in the ethylene molecule, this carbon atom is in the $sp^2$ hybridization. These bonds lie in the same plane, and the bond angle between them is 120°. The non-hybridized cloud of the *p*-electron from the carbon atom and the *p*-electron cloud from the oxygen atom (the other electron of this atom is involved in the formation of the σ bond between the carbon and oxygen) form the π bond by lateral overlapping (Fig. 44).

It can be seen that there is much in common between the electron structures of the double bond in the molecules of aldehyde and ethylene. But there are also differences. As distinct from ethylene, the double bond in the aldehyde is established between two atoms with different electronegativities, and it is therefore polar. The electron density (mainly of the π bond, since it is more mobile) is displaced from the carbon to the oxygen atom and, hence, one of them becomes partly positive and the other, partly negative. The electron structure of aldehydes can therefore be expressed by the formula




It can be seen from Table 7.1 that only the first member of the series, formaldehyde, is a gas. Next follow liquids and then solids. The first members are soluble in water, but as the molecular weight of the substances increases, their solubility decreases; the higher aldehydes are insoluble in water.

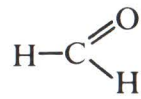
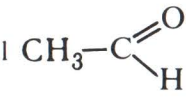
As distinct from alcohols, aldehydes do not form hydrogen intermolecular bonds, because the positive charge on the hydrogen of the aldehyde group is too small (because of the low polarity of the C—H bond) to establish such a bond with the negatively charged oxygen atom of another aldehyde group. The boiling points of the aldehydes are therefore lower than those of alcohols with the same number of carbon atoms in the molecule. The solubility in water of the first members of the homologous series can be explained by the establishment of the hydrogen bonds with water molecules through their hydrogen atoms. Draw a diagram of formation of these bonds between molecules of formaldehyde and water.

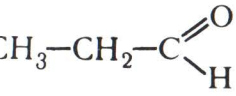
The names of the aldehydes are derived from the acids into which they are oxidized. Formic aldehyde (formaldehyde) owes its name to formic acid into which it is oxidized; acetic aldehyde (acetaldehyde) is named after acetic acid, etc.

Formaldehyde is a gas with a suffocating pungent odour. It is a strong poison. A 40-per cent aqueous solution of formaldehyde is known as *formalin.*

Aldehydes are named in the IUPAC system by dropping the ending *-e* and

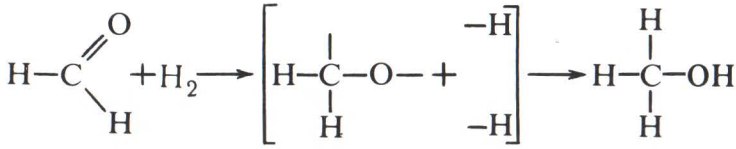
adding the suffix *-al* to the name of the parent hydrocarbon, for example:

methanal  , ethanal 

propanal 

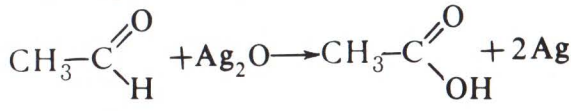
Chemical Properties. The chemical properties of aldehydes primarily depend on the presence of the carbonyl group in their molecules. Addition reactions may occur at the double bond.

If, for example, formaldehyde and hydrogen are passed over a hot nickel catalyst, the hydrogen is attached to the formaldehyde, reducing it to methyl alcohol. This can be shown schematically as



This equation is also valid for some other aldehydes.

Because of the carbonyl oxygen, aldehydes are readily oxidized at the C—H bond of the aldehyde group. If an ammoniacal solution of silver oxide, which is an oxidant ($Ag_2O$)*, is placed in a clean test tube and aldehyde is added, and the mixture is then heated carefully, a silver deposit is formed on the test tube walls. The aldehyde is converted in this oxidation-reduction reaction into the acid (an ammonium salt is formed because of the presence of excess ammonia), while the silver is precipitated in the free state:



Acetic acid

This is the *silver mirror reaction.*

Copper hydroxide $Cu(OH)_2$ can also be used as an oxidant of aldehydes. If an aldehyde solution is added to cupric hydroxide and the mixture is heated, a yellow substance CuOH is first precipitated, which is then converted into cuprous oxide $Cu_2O$. The cupric hydroxide oxidizes the aldehyde to the acid, and is itself reduced to copper(I) oxide.

The reaction can be written in a general form as follows:

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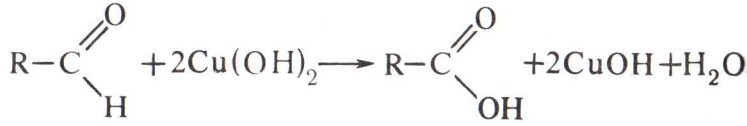
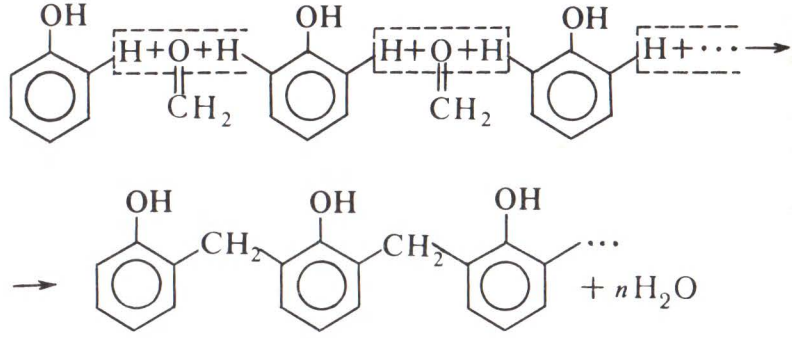
* The oxide of monovalent silver is insoluble in water. It reacts with ammonia to give a soluble compound $Ag(NH_3)_2OH$.



$$2CuOH \longrightarrow Cu_2O + H_2O$$

The reactions with the ammoniacal solution of silver (I) oxide and copper (II) hydroxide can be used to detect aldehydes.

In addition to these reactions, which are common to all aldehydes, there are also some important reactions specific for a few individual aldehydes. Consider the interaction of formaldehyde with phenol as an example. If a mixture of these two substances is heated in the presence of an acid or alkali, a high-molecular product, phenol-formaldehyde resin, is produced. The reaction can be shown schematically as this



Another product of this reaction is water.

All the reactions we considered earlier, by which high-molecular substances can be prepared, were addition polymerization reactions. The reaction of phenol with formaldehyde is another type of polymerization reactions. It is called *condensation polymerization* (polycondensation) *reaction.*

●Condensation polymerization is the reaction of formation of high-molecular substances with liberation of a low-molecular side-product.

Uses of Aldehydes. Formaldehyde and acetaldehyde are the most used aldehydes nowadays. Formaldehyde is usually used as an aqueous solution, called formalin. Many of its uses are based on its ability to coagulate proteins.

Formaldehyde is a popular disinfectant. In agriculture it is used to treat seeds. Formalin is widely used in leather tanning: it makes leather hard and protects it from decay. Formalin is also used for making biological preparations. The reaction between formaldehyde and ammonia gives a popular medicinal preparation, urotropine.

But the most formaldehyde is used for the manufacture of phenol-formaldehyde resins. Mixtures of phenol-formaldehyde resin, filling materials (sawdust, cotton fabrics, etc.) and other substances make valuable plastics that can be pressed into various shapes. The material is filled into moulds under pressure and high temperature. There the linear molecules of the resin react to form

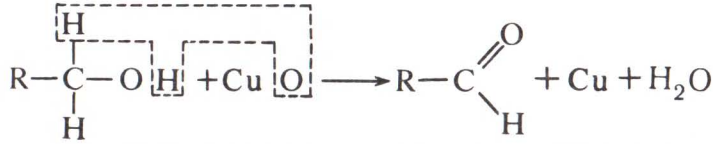
polymers with spatial structures. The material loses its thermal plasticity, and becomes strong and insoluble.

Phenol-formaldehyde resins are used for making various heavy-duty machine parts, pulleys, parts of rectifying columns, etc. In addition to their high wear resistance (higher than that of metal) parts made from phenol-formaldehyde resin do not make much noise.

Acetaldehyde is also used in large quantities for the manufacture of acetic acid. Ethyl alcohol is obtained by reducing acetaldehyde in some countries.

Preparing Aldehydes. The general method for obtaining aldehydes is the oxidation of alcohols. In order to understand this process better, carry out the following experiment.

Heat a copper spiral in the flame of a burner and put it into a test tube containing alcohol: the copper wire, that became covered with a dark coat of copper (II) oxide during heating, becomes now clean again. An odour of the aldehyde can be smelt:



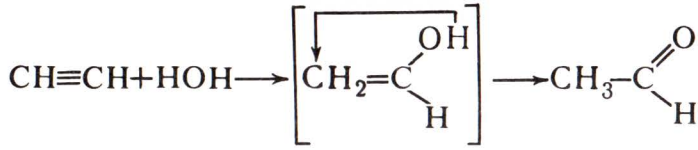
This reaction is used for the industrial preparation of formaldehyde when a mixture of vapours of methyl alcohol and air passes over a hot copper (or silver) gauze.

Other oxidants (potassium permanganate, for example) can also be used in the laboratory for oxidation of alcohols into the corresponding aldehydes. Designate the oxidant as O and write the equation for the reaction by which acetaldehyde is prepared from the corresponding alcohol.

During the oxidation of alcohols, two hydrogen atoms are eliminated from their molecules (see the reaction equation). An aldehyde is thus formed by the dehydrogenation of an alcohol. Hence, the name aldehyde, for which the first two letters are borrowed from the word alcohol (*al*) and the remaining letters are the modification of dehydrogenation: alcohol deprived of its hydrogen.

Acetaldehyde is produced in industry mainly by the reaction suggested by the Russian scientist Kucherov in 1881. In it acetylene is hydrated in the presence of mercury salts.

Water is first attached to acetylene at the site of one $\pi$ bond to form vinyl alcohol (remember the structural formula of the vinyl radical). However, unsaturated alcohols, in which the hydroxyl group is attached to the carbon atom connected to the double bond, are unstable and readily isomerized. Vinyl alcohol is therefore easily converted into the aldehyde:



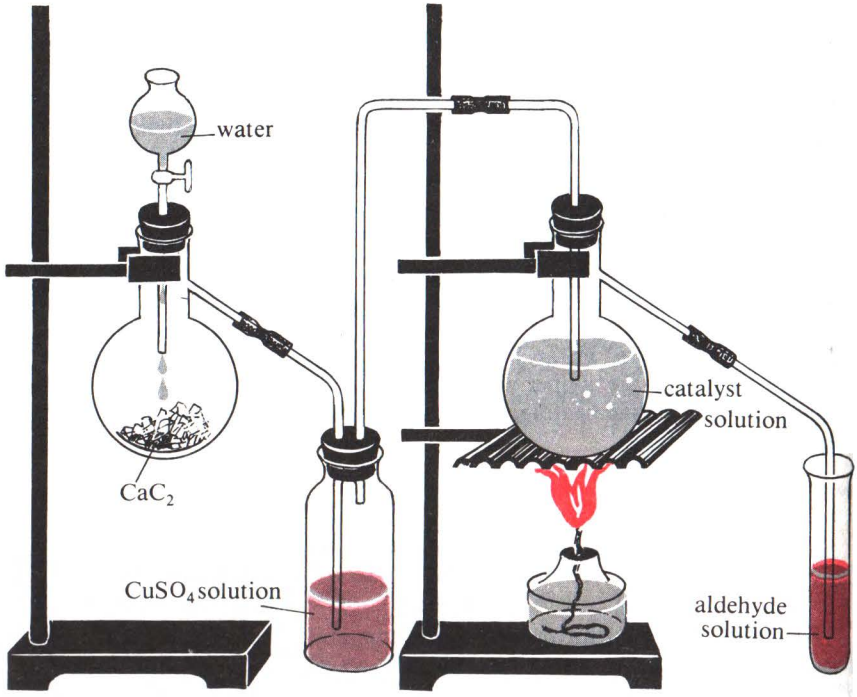



Fig. 45. Preparing acetaldehyde by hydration of acetylene

The reaction is easy to realize by passing acetylene into hot dilute sulphuric acid containing mercury (II) oxide (Fig. 45). Acetaldehyde will be found in the receptacle a few minutes later.

Industrial manufacture of the acetaldehyde by this method has a disadvantage: mercury compounds are poisonous.

A new method of preparing acetaldehyde by the oxidation of ethylene with oxygen in the presence of palladium chloride and copper chloride has been recently used. Without going into too much detail, the reaction can be expressed by the following summary equation:

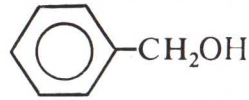
$$2CH_2{=}CH_2{+}O_2 \rightarrow 2CH_3{-}C\overset{O}{\underset{H}{<}}$$

This method is believed to be more advantageous because ethylene is now easily available and far less expensive than acetylene (why?).

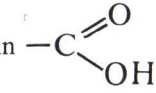
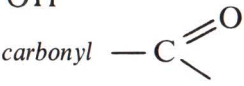
? △ 1. Following the IUPAC system, name the following aldehydes:

$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}C\overset{O}{\underset{H}{<}}$$

$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}{-}CH_2{-}C\overset{O}{\underset{H}{<}}$$

2. How can ethyl bromide be obtained from acetaldehyde in two stages? Write down the equations for the reactions.
3. What quantity of propionic aldehyde (in grams) will be oxidized in the silver mirror reaction when 0.01 mole of silver is reduced?
4. How can copper(II) hydroxide be used to differentiate between glycerol and acetaldehyde?
5. How can ethyl alcohol be obtained from acetylene by two methods? Write down the reaction equations and specify the conditions for the reactions.
6. Like ethylene, formaldehyde can be polymerized at the double bond. Polyformaldehyde is produced by this reaction, in which carbon and oxygen atoms alternate in the chain. The polymer has good mechanical properties and is used for making machine parts, films, fibres, etc. Write down the scheme for the polymerization of formaldehyde, the formula of the repeat unit and the formula of the polymer produced.
7. What is common and what is different in addition and condensation polymerization reactions?
8. The weight of a macromolecule prepared by addition polymerization is equal to the sum of the parent molecules. Does this rule hold for substances obtained by condensation polymerization? Explain your answer.
9. Aromatic alcohols can be converted into aldehydes like common alcohols. Write down the equation for oxidation of benzyl alcohol  to benzaldehyde. Can phenols be converted into aldehydes in this way? Explain your answer.
10. Formaldehyde that was produced by the oxidation of 2 moles of methyl alcohol was dissolved in 100 g of water. What is the formaldehyde concentration in the solution?

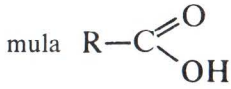
## 7.2 Monocarboxylic Acids

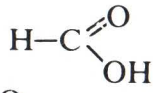
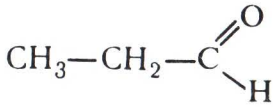
Structure and Physical Properties. When we wrote structural formulas of acids during the study of properties of aldehydes, you might have noticed that they contain  group. This is called the *carboxyl group*. It derives its name from *carbonyl*  and *hydroxyl* —OH.

● Carboxylic acids are organic substances whose molecules contain one or several carboxyl groups , attached to the hydrocarbon radical*.

Depending on the number of carboxyl groups in the molecule, carboxylic acids have the prefixes mono-, di-, tri-, etc. Table 7.2 gives examples of monocarboxylic acids.

* The carboxyl group is connected to the hydrogen atom in the molecule of formic acid, the first member of the homologous series.

The structure of monocarboxylic acids can be expressed by the general formula  or R—COOH. Models of molecules of some carboxylic acids are shown in Appendix, in Fig. IV.

In the IUPAC system, carboxylic acids are named by dropping the *-e* and adding the suffix *-oic* to the name of the parent hydrocarbon containing the same number of carbon atoms. The resulting name is then followed by *acid*, e.g. methanoic acid  (formic acid), propanoic acid  (propionic acid), etc. The trivial names of carboxylic acids are, however, more popular.

As distinct from the aldehydes, there are no gaseous carboxylic acids (see Table 7.2). The lower members of the series are all liquids with pungent odour

*Table 7.2*

HOMOLOGOUS SERIES OF THE MONOCARBOXYLIC ACIDS

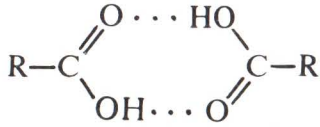
| Acid | Formula | B.p., °C |
|---|---|---|
| Formic acid | H—COOH | 101 |
| Acetic acid | $CH_3$—COOH | 118 |
| Propionic acid | $CH_3$—$CH_2$—COOH | 141 |
| Butyric acid | $CH_3$—$CH_2$—$CH_2$—COOH | 163 |
| Valeric acid | $CH_3$—$CH_2$—$CH_2$—$CH_2$—COOH | 186 |
| Caproic acid | $CH_3$—$(CH_2)_4$—COOH | 205 |
| Enanthic acid | $CH_3$—$(CH_2)_5$—COOH | 223 |
| . . . . . | | |
| Palmitic acid | $CH_3$—$(CH_2)_{14}$—COOH | solid |
| Margaric acid | $CH_3$—$(CH_2)_{15}$—COOH | solid |
| Stearic acid etc. | $CH_3$—$(CH_2)_{16}$—COOH | solid |

and are readily soluble in water. As the molecular weight increases, the solubility decreases. Acids with higher molecular weights are odourless solids insoluble in water.

The absence of gaseous substances in the homologous series was already discussed when we studied alcohols, and we know the reason. It can be supposed that the absence of gaseous carboxylic acids is due to the association of molecules through hydrogen bonds.

In fact, the determination of the molecular weights of the liquid acids shows that they exist as paired molecules or dimers. Formic acid, even in the vapour state, is composed of dimers. Acetic acid vapour is a mixture of single and paired molecules.

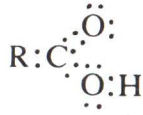
The structure of a carboxylic acid dimer can be shown like this:



Two hydrogen bonds are established between two molecules. This accounts for the comparatively high strength of the dimers.

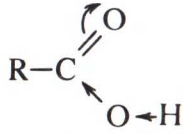
We explained earlier the solubility of alcohols in water by the formation of hydrogen bonds with water. The situation is the same for carboxylic acids. The solubility in this case also decreases with increasing molecular weight, i.e. with increasing hydrocarbon radical of the molecule.

Once we know the electron structure of the alcohols and aldehydes we can describe the electron structure of the carboxylic acids, because the functional group includes both the carbonyl and the hydroxyl groups:



The electron structure of carboxylic acids should explain why they are acidic (a proton can be easily eliminated).

The structure of the carboxylic acids differs from that of the alcohols by the appearance of the oxygen atom instead of two hydrogen atoms. The properties of the hydroxyl hydrogen have probably changed under the effect of the carbonyl oxygen. When we discussed the aldehydes, we saw that the electron density of the C=O bond (especially of the $\pi$ bond) was displaced towards oxygen, the more electronegative element. As a result, the carbon atom of the carbonyl group acquires a partial positive charge. In order to compensate for this, the carbon atom attracts the electrons of the hydroxyl oxygen. For the same reason, this oxygen attracts the electron density of the O—H bond; its polarity increases and the hydrogen is more easily eliminated as the proton. This shift of the electrons is shown in formulas by arrows:



**Chemical Properties.** Unlike alcohols, water-soluble acids have a specific sour taste, they turn blue litmus paper red, and conduct electricity. Their dissociation in aqueous solutions can be represented by the equation:

$$R—COOH \rightleftarrows H^+ + R—COO^-$$

Comparing the degree of dissociation, it can be seen that only formic acid is an electrolyte of medium strength while the other acids are weak electrolytes, the degree of dissociation decreases as the molecular weight increases.

Some metals react with the acid solutions to liberate hydrogen and form salts, e.g.:

$$2CH_3—COOH + Mg \rightarrow H_2 + Mg(CH_3COO)_2$$

Magnesium acetate

The ionic equation* of this reaction is

$$2CH_3COOH + Mg \rightarrow H_2 + Mg^{2+} + 2CH_3COO^-$$

The hydrogen is liberated here more slowly than in the reactions between metals and strong acids (such as sulphuric or hydrochloric acid).

Carboxylic acids react with basic oxides and bases to give salts:

$$CH_3—CH_2—COOH + NaOH \rightarrow CH_3—CH_2—COONa + H_2O$$

Sodium propionate

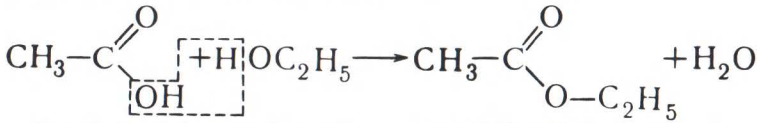
Or in the ionic form:

$$CH_3—CH_2—COOH + Na^+ + OH^- \rightarrow H_2O + Na^+ + + CH_3—CH_2—COO^-$$

Carboxylic acids react with salts to displace weaker and more volatile acids. Write down the equation for the reaction between acetic acid and calcium carbonate. The reaction yields calcium acetate, carbon dioxide, and water.

Carboxylic acids enter reactions which we didn't consider in inorganic chemistry.

Place acetic acid in a test tube and add ethyl aclohol. No signs of reaction will at first be seen. If sulphuric acid is now added and the mixture heated, a pleasant odour of ethyl acetate will soon be felt:



As distinct from ethers (see page 106), ethyl acetate is an *ester*.

All properties of acids, that we have learnt earlier, are due to the presence of the hydroxyl group in their molecules. Does the carbonyl group retain here its properties?

Addition reactions at the C=O double bond readily occur in aldehydes. Experiments show that addition reactions are not very likely to occur at the carbonyl group since the double bond here is more stable. Hydrogen, for example, can be attached, but only under more rigorous conditions than in the case with aldehydes.

This change in the properties of the C=O bond is due to the presence of the hydroxyl group in the molecule: the shift of the electrons from the hydroxyl group to the carbon atom partly neutralizes its positive charge, which, in turn, affects the reactivity of the carbonyl group. This is another proof that the atoms in molecules affect each other.

There is another site in a carboxylic acid where chemical reactions are likely to occur: this is the hydrocarbon radical. The halogens can be substituted here

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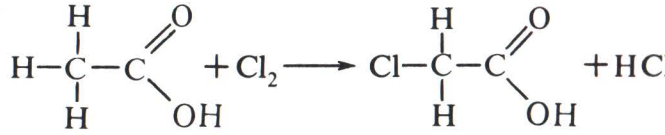
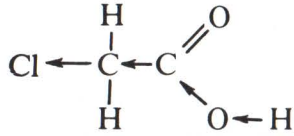
* Carboxylic acids that are weak electrolytes will be expressed in the molecular form as in inorganic chemistry.

for the hydrogen atoms. The substitution is especially easy at the hydrocarbon link nearest the carboxyl:

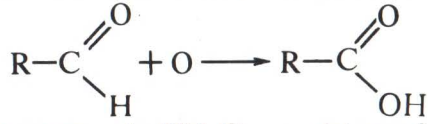


Chloroacetic acid

The incorporation of the halogen atoms into the acid molecule has some consequences: the dissociation degree of the acid increases strongly. Chloroacetic acid, for example, is 100 times stronger than acetic acid. Consider the diagram below and try to explain why the incorporation of the chlorine atom makes the acid stronger

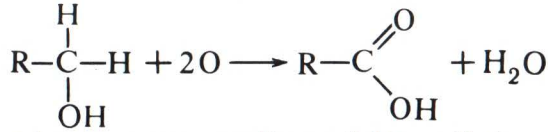


**Preparing Carboxylic Acids.** The general method for obtaining carboxylic acids is the oxidation of the corresponding aldehydes:



Potassium permanganate $KMnO_4$, a mixture of potassium dichromate $K_2Cr_2O_7$ and concentrated sulphuric acid, and less strong oxidants can be used for the purpose.

Since aldehydes are formed by oxidation of alcohols, acids can, in fact, be obtained directly by oxidation of alcohols without isolating the intermediate aldehydes. This oxidation can be expressed by the following total equation:



Since hydrocarbons are now readily available, oxidation of saturated hydrocarbons is widely used for the manufacture of carboxylic acids.

? △

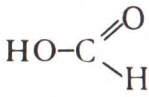
1. The simplest dicarboxylic acid is oxalic acid HOOC—COOH (found in sorrel). Can it be regarded as a homologue of formic acid? Explain your answer.
2. How do we know that the carbon atom of the carboxyl group is in the $sp^2$ hybrid state? How does this influence the spatial structure of the carboxyl group?
3. Write down the equations for reactions of oxidation of (a) formaldehyde, and (b) propionic aldehyde to the corresponding acids.

4. Write down equations for the reactions of formic acid with (a) zinc, (b) potassium hydroxide, and (c) soda. By what signs can it be established that the reaction has occurred in each case?
5. 0.1 mole of a carboxylic acid was neutralized by 8 g of sodium hydroxide. Determine the number of the carboxyl group in the acid and write down its structural formula if its molecular weight is 104.
6. What experiments will show that the carbonyl and hydroxyl groups affect each other in carboxylic acids? Use the electron theory to explain your answer.
7. When we studied the mechanism of the addition reactions of unsaturated hydrocarbons, we mentioned that the hydrocarbon radical can displace the electrons to the carbon atom at the double bond. The dissociation degree of the acetic acid is lower than that of the formic acid. Does this agree with the appearance of the methyl radical in the acid molecule? Explain your answer.
8. In which of the following pairs of acids will the dissociation degree be higher: (a) chloroacetic or trichloroacetic; (b) trichloroacetic or trifluoroacetic acids? Explain your answer.
9. Which acid is stronger, chloroacetic $ClCH_2—COOH$ or chlorobutyric $ClCH_2—CH_2—CH_2—COOH$? Explain your answer.

## 7.3 Homologous Series of Monocarboxylic Acids

Formic Acid. This is the first member of the homologous series of saturated acids. It is contained in the excretions of ants, stinging nettles, and the needles of conifer trees.

It is the strongest monocarboxylic acid. But it has some other special features. Consider its structure (Fig. 46). The formula of the acid can be represented in such a way that the aldehyde group will be seen in the acid molecule



. In fact, formic acid has some of the properties of aldehydes (in addition to typical acid properties). It is, for example, readily oxidized by the ammoniacal solution of silver(I) oxide. Write down the equation for this reaction. What substances are formed by the oxidation of formic acid?

The formic acid is used industrially as a reducing agent, because it is readily oxidized. It reacts with alcohols to give esters that are used as solvents (e.g. ethyl formate) and to yield substances used in perfume (e.g. amyl formate).

Acetic Acid. Acetic acid is found in plants and animal excretions; it is formed by the oxidation of organic substances. The model of its molecule is given in Fig. IV.

Acetic acid is most widely used carboxylic acid. An aqueous solution of acetic acid is known as vinegar and is used for pickling fruits and vegetables, and as a condiment.

The salts of acetic acid, *acetates*, are prepared by various salt-forming reactions. Various esters are obtained by the reaction of the acid with alcohols. Like the esters of formic acid, they are used as solvents and scents. Acetic acid is used in the manufacture of acetate fibre, dyes (e.g. indigo), medicines (e.g. aspirin), etc.

Some derivatives of acetic acid are used in agriculture to control weeds.

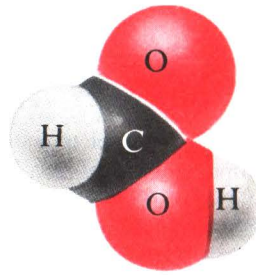
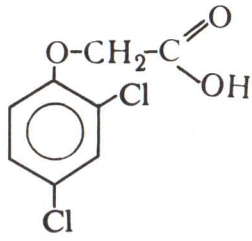



Fig. 46. A model of a molecule of formic acid

Substances used to fight weeds are called weed killers. The most popular weed killers are those based on 2,4-dichlorophenoxyacetic acid (2,4-D), which has the structure




2,4-Dichlorophenoxyacetic acid

A combination of phenyl with oxygen, $C_6H_5O$, is called the phenoxy group. The molecule above also contains two chlorine atoms in the ring at positions 2 and 4, hence the name 2,4-dichlorophenoxyacetic acid.

The salts and other derivatives of this acid are used as weed killers, e. g. its sodium salt. Write down its structural formula.

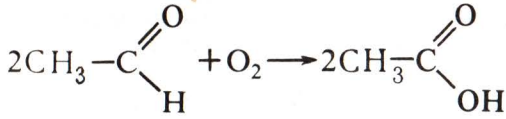
These substances are especially effective against dicotyledonous plants that grow together with cereals.

The sodium salt of 2-methyl-4-chlorophenoxyacetic acid (MCP) is also a popular weed killer. It differs from the sodium salt of 2,4-dichlorophenoxyacetic acid in that it has a methyl group instead of one chlorine atom in the phenyl radical. Write down its structural formula.

The first method used to prepare acetic acid was the natural fermentation of wine. Under the action of bacterial enzymes, the alcohol is oxidized by the atmospheric oxygen into acetic acid:

$$CH_3—CH_2—OH + O_2 \rightarrow CH_3—COOH + H_2O$$

As technology advanced, a method was devised for producing acetic acid by thermal decomposition of wood. Methyl alcohol, acetone, and acetic acid are contained in the liquid products of this process. The acid can be isolated from the mixture as an acetate (e. g. calcium acetate), from which the pure acid is finally obtained. Acetic acid can be synthesized by oxidation of acetaldehyde using the oxygen of the air in the presence of a catalyst



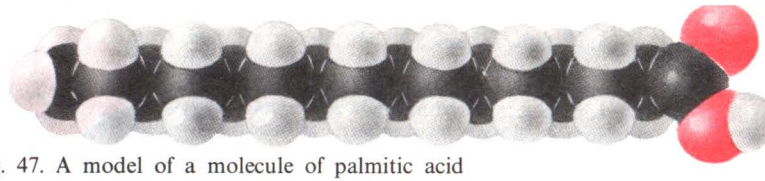


Fig. 47. A model of a molecule of palmitic acid

Try to remember the industrial method for preparing acetaldehyde. If we assume that acetylene is produced from methane, then the whole chain of consecutive conversions, by which the raw material is converted into acetic acid, can be represented as follows:

$$CH_4 \longrightarrow C_2H_2 \longrightarrow CH_3{-}C(=O){-}H \longrightarrow CH_3{-}C(=O){-}OH$$

At present the most popular method of obtaining acetic acid is the oxidation of butane by atmospheric oxygen:

$$2CH_3{-}CH_2{-}CH_2{-}CH_3 + 5O_2 \longrightarrow 4CH_3COOH + 2H_2O$$

The reaction gives a mixture of substances from which the end product, acetic acid, is recovered.

Palmitic and Stearic Acids. The most important monocarboxylic acids with higher molecular weights are palmitic acid $CH_3{-}(CH_2)_{14}{-}C(=O){-}OH$ and stearic acid $CH_3{-}(CH_2)_{16}{-}C(=O){-}OH$. They are contained as esters of glycerol in plant and animal fats.

Palmitic and stearic acids are white solids insoluble in water. The hydrocarbon radicals of their molecules contain an unbranched chain of 15 and 17 carbon atoms, respectively, connected by σ bonds (Fig. 47).

These acids enter the same reactions as other carboxylic acids. When they react with alkali solutions, or sodium carbonate, they form salts

$$C_{15}H_{31}COOH + NaOH \rightarrow C_{15}H_{31}COONa + H_2O$$

$$2C_{17}H_{35}COOH + Na_2CO_3 \rightarrow 2C_{17}H_{35}COONa + H_2O + CO_2$$

The sodium salts of these acids (palmitates and stearates) are soluble in water. They are detergents and are the essential components of hard soaps.

The potassium salts of the acids are liquid soaps, and are often used in medicine.

The sodium salts contained in soaps can be converted back into the acids by

acting with a strong acid on their aqueous solutions, e.g.:

$$C_{17}H_{35}COO^- + Na^+ + H^+ + HSO_4^- \rightarrow C_{17}H_{35}COOH + Na^+ + HSO_4^-$$

The calcium and magnesium salts of higher homologues of carboxylic acids are insoluble in water. The washing properties of ordinary soaps are lost in hard water because these salts are precipitated.

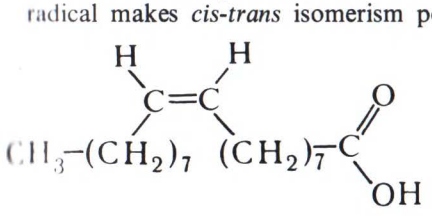
Write down the formulas of the insoluble salts of stearic acid by analogy with the formulas given above.

Oleic Acid. It is a representative of unsaturated monocarboxylic acids. There are acids whose hydrocarbon radicals have one or more double bonds between the carbon atoms.

The homologous series of unsaturated acids with one double bond begins with acrylic acid $CH_2=CH-C\begin{matrix}O\\ \diagdown\\ \diagup\\ OH\end{matrix}$, which can be regarded as a derivative of propylene. We shall now consider in more detail a higher member of the homologous series of unsaturated acids, oleic acid $C_{17}H_{33}COOH$, or $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$. Together with palmitic and stearic acids it is present as an ester of glycerol in fats.

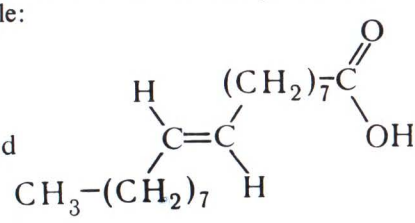
A molecule of oleic acid has a double bond in the middle of its carbon chain. The change in the structure has influenced its properties: as distinct from stearic acid, oleic acid is a liquid.

This can be explained as follows. The double bond in the hydrocarbon radical makes *cis-trans* isomerism possible:



*cis*-isomer

and



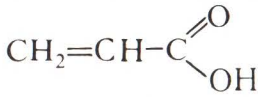
*trans*-isomer

Oleic acid is the *cis*-isomer. The configuration of its molecule is such that the intermolecular forces are comparatively insignificant and the substance exists as a liquid. The molecules of the *trans*-isomer are elongated, and pack together closely so that the intermolecular forces become more effective and the substance becomes solid. This is called elaidic acid.

In addition to the carboxyl group, oleic acid also has a double bond, and can enter reactions specific not only for acids, but also for unsaturated compounds, i.e. it has a *dual chemical character*, being an acid and an unsaturated hydrocarbon. It can attach bromine and hydrogen at the double bond. In the latter case, oleic acid is converted into stearic acid:

$$C_{17}H_{33}-C\begin{matrix}O\\ \diagdown\\ \diagup\\ OH\end{matrix} + H_2 \longrightarrow C_{17}H_{35}-C\begin{matrix}O\\ \diagdown\\ \diagup\\ OH\end{matrix}$$

? △

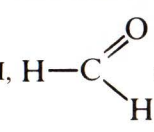
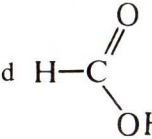
1. How can the weakness of acetic acid be proved experimentally?
2. Write down the equations for the reactions by which acetic acid is prepared from (a) calcium carbonate, (b) methane.
3. How can ethane be converted into (a) an ether, (b) an ester? Give the reaction equations.
4. How can acetic acid be prepared from ethylene? Give the reaction equations.
5. Write down the ionic equations for the reactions between (a) sodium stearate and sulphuric acid, (b) sodium palmitate and calcium bicarbonate. Which phenomenon can be explained by the last reaction?
6. How can the washing properties of soap in hard water be improved? Explain your answer.
7. The addition of hydrogen bromide to acrylic acid  at the double bond contradicts the Markownikoff rule. Write down the reaction equation and explain your answer.
8. Explain why the first member of the series of unsaturated monocarboxylic acids must have at least three carbon atoms. Write down the equations for the reactions in which this acid can participate.
9. Oleic acid discolours bromine water. Write down the reaction equation.

■

10. Carry out the following experiments at home: (a) try acetic acid on chalk, soda, or some metals; (b) does acetic acid change the colour of vegetable juices? (c) determine the dilution at which you cannot taste the acidity of acetic acid.

## 7.4 Links Between Hydrocarbons, Alcohols, Aldehydes, and Acids

We have already discussed the links between the hydrocarbons and the alcohols. Hydrocarbons can be converted into their halogen derivatives, and the halogen derivatives can be converted into alcohols. When we studied other classes of compounds, we learned that alcohols could be converted into aldehydes, and aldehydes into carboxylic acids. We have thus discussed classes of compounds from hydrocarbons to acids and can state that they are closely related, each class being a more complicated variation of the previous class.

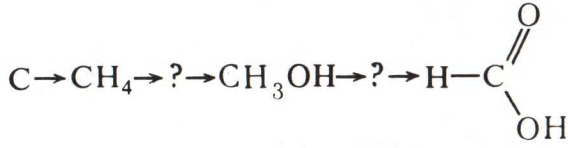
Alcohols, aldehydes, and carboxylic acids can be regarded as the products of the consecutive oxidation of hydrocarbons. If we compare the composition of these compounds, for example, $CH_4$, $CH_3OH$,  and  , we can see that the oxygen content (in per cent) increases, i.e. each next compound has a higher degree of oxidation than the previous one. The same

conclusion can be made from the electron theory viewpoint: when a methane molecule is converted into a molecule of the alcohol, one valency electron of the carbon atom is displaced toward the oxygen atom; during the formation of a molecule of an aldehyde, the oxygen atom attracts two electrons of the carbon atom, and in the molecule of formic acid, the oxygen atoms attract three electrons, i. e. the carbon atom is oxidized in steps. It is easy to see that further oxidation will finally give carbon dioxide, in which all the valency electrons of carbon will be displaced toward the oxygen atoms.

These classes do not cover all organic compounds. The carboxylic acids and the other substances can be converted into new classes thus increasing the variety of organic compounds. All of these can be considered as derivatives of the hydrocarbons. But since hydrocarbons can be produced from carbon and hydrogen, or from inorganic compounds, we can say that all the substances occurring in nature, both inorganic and organic, are united together.

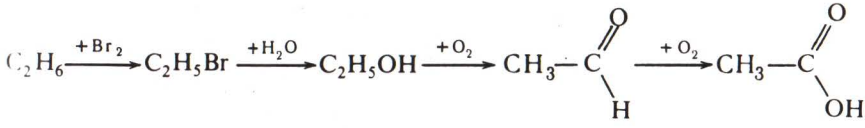
?

1. Write down the equations for the following conversions:

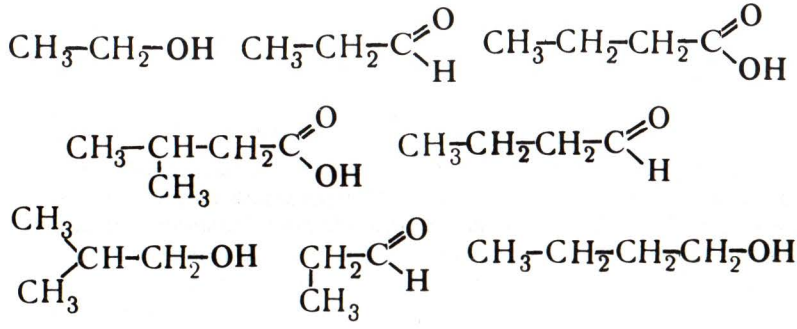


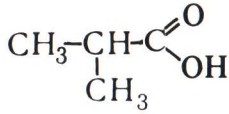
△

2. Write down the equations for reactions by which the following conversions can be realized:



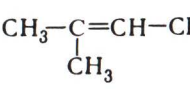
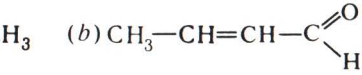
3. The carboxylic acids are often prepared in the laboratory by the direct oxidation of the alcohols, without isolating the aldehydes. Write down the equations for the preparations of acetic and propionic acids by the oxidation of the corresponding alcohols.
4. Classify all the organic and inorganic acids that you know according to various signs. Give examples.
5. Consider the formulas given below and write out (a) formulas of homologues, (b) formulas of isomers:





$CH_3OH$

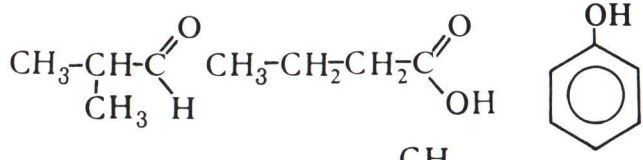
6. How can the following conversions be realized: $CH_4 \rightarrow ? \rightarrow ? \rightarrow \rightarrow CH_3COOH$? Write down the reaction equations and specify the reaction conditions.
7. Consider the formulas of substances given below and decide which of them can have *cis-trans* isomers?

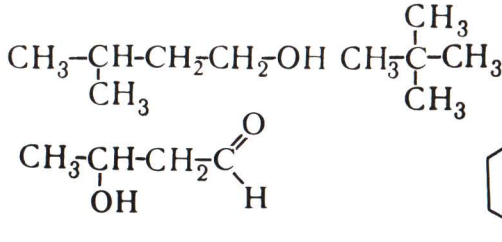
(*a*)  (*b*)  (*c*) $CH_2=CH-CH_2OH$

d) HOOC—CH=CH—COOH

Write down the formulas of the *cis*- and *trans*-isomers.

8. In which of the substances given below, hydrogen bonds are formed between the molecules: (a) $C_6H_6$; (b) $C_6H_5OH$; (c) $C_6H_{14}$; (d) $HOCH_2—CH_2OH$; (e) HCOOH? How are the properties of these substances affected by the hydrogen bonding?
9. Which of the substances given below will react with (a) sodium, (b) sodium hydroxide? Write down equations for the reactions.





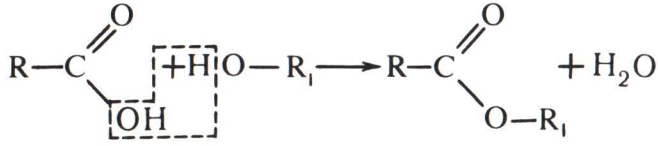
10. By what reactions can heptane be converted into benzoic acid $C_6H_5—COOH$? Give the reaction equations and specify the conditions for the reactions.

# 8 Esters. Fats

When we studied the carboxylic acids, we mentioned their derivatives, the esters, several times. Let us now discuss them in more detail. We shall also discuss the chemistry of fats, which are biologically important substances.

## 8.1 Esters

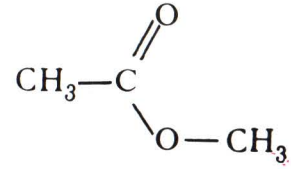
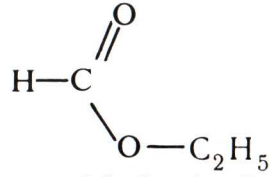
Manufacture of Esters and Their Structure. We already know that esters are formed by reactions between acids and alcohols. In a general form this can be expressed as



Acid Alcohol Ester

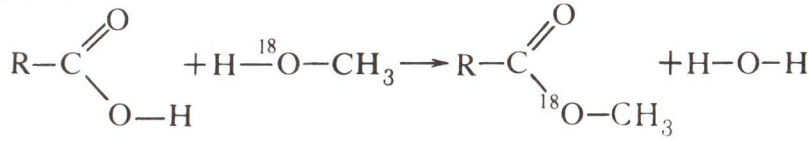
●The formation of an ester by the reaction of an acid with alcohol is called esterification.

The reactions often require the presence of a strong mineral acid because the hydrogen ion acts as a catalyst.

When naming an ester, the name of the alcohol is given first and followed by the name of the acid. For example, methyl formate  ethyl formate  , etc.

Since the hydrogen of the functional carboxyl group in acids is more labile than in the alcohols, we might expect that during esterification, the hydrogen atom would be eliminated from the acid molecule, and the hydroxyl group, from the alcohol molecule. The reaction scheme given above would then be incorrect. The actual esterification reaction scheme was established by tracing it with labelled atoms.

A carboxylic acid was reacted with an alcohol, which contained the heavy isotope of oxygen (oxygen 18, instead of the normal oxygen with the atomic weight 16):



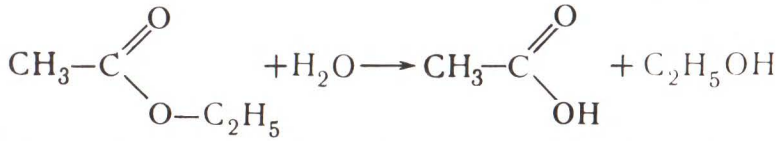
The heavy isotope of oxygen was then detected in the resultant ester. This indicates that during the esterification, only the hydrogen atom (and not the hydroxyl group) is eliminated from the alcohol molecule, while the hydroxyl group is eliminated from the acid molecule.

The esterification mechanism is in fact much more complicated than the elimination of water components from the molecules of alcohol and acid and the combination of the formed particles. However, only the result of the reaction is important for us at this stage of our studies; the mechanism is discussed in detail in more complete courses of organic chemistry.

Physical Properties of Esters and Their Occurrence in Nature. The esters of the monocarboxylic acids are usually liquids with pleasant odours. Ethyl formate smells of rum and ethyl butyrate of pineapple.

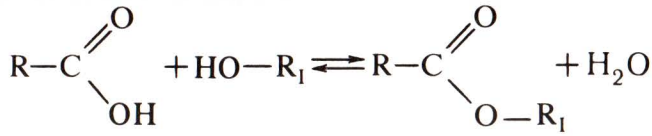
The odours of flowers, fruits, and berries mostly depend on the presence of esters in them. The main use of esters is for scents. Synthetic esters in the form of fruit oils are used (together with other aromatic substances) in soft drinks, as flavouring additives for sweets, in perfumery, and so on. Some esters (e. g. ethyl acetate) are used as solvents.

Chemical Properties. The important chemical property of esters is their reaction with water. If an ester, for example ethyl acetate, is heated with water in the presence of a mineral acid, acetic acid and ethyl alcohol are formed:



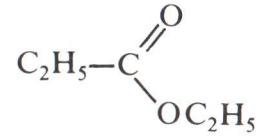
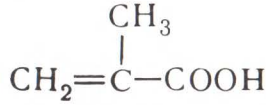
This reaction is known as *hydrolysis*. It is the reverse of esterification. Therefore, if a mixture of an alcohol and a carboxylic acid is heated, not only the esterification reaction occurs, but also the hydrolysis of the resultant ester. The esterification is thus reversible. The rate of the reverse reaction during esterification increases as the quantity of ester and water increases. Finally the rates of the esterification and hydrolysis reactions come into equilibrium, and the quantity of ester in the mixture stops increasing.

This can be shown as follows:



In order to displace the equilibrium of this reaction in the direction of the ester formation, the reaction between the products has to be prevented, for example, by distilling the ester or by binding the water with a dehydrating agent.

If, on the contrary, the ester is to be hydrolyzed, i.e. it has to be decomposed into the parent acid and the alcohol by reacting it with water, the reaction should be carried out in the presence of alkali. The alkali will convert the acid into its salt and prevent it from reacting again with the alcohol. The acid can then be recovered from the salt.

1. Write down the equation for the esterification of (a) acetic acid and 3-methylbutanol-1, (b) butyric acid and propanol-1. Characterise the properties of the resultant esters.
2. Name the following esters: (a)  , (b) $HCOOC_3H_7$.
3. Write down the equations for the reactions by which (a) methyl formate is obtained from methane, (b) ethyl acetate is obtained from ethylene.
4. Methyl ester of methacrylic acid  is easily polymerized into a high-molecular product known as "Plexiglas". Write down (a) the equation for the reaction by which the ester is prepared from methacrylic acid and methyl alcohol, (b) the equation for the polymerization of the ester, if it is known that the polymerization occurs at carbon-carbon double bond.
5. We have already discussed the isomerism between alcohols and ethers. Likewise there exists isomerism between the monocarboxylic acids and esters (with the same number of carbon atoms in the molecule). Write down the formulas of all the isomeric acids and esters having the formula $C_5H_{10}O_2$.
6. Two isomers have vapours with densities of 30 (relative to hydrogen). One of them is hydrolyzed to give two oxygen-containing compounds while the other readily reacts with alcohols (esterification). Write down the structural formulas of these substances and the equations for the reactions that were mentioned.
7. A colourless liquid with the molecular formula of $C_3H_6O_2$ does not react with sodium metal, but when heated with a solution of sodium hydroxide, it gives the salt, sodium acetate. To what class does this substance belong? Draw its structural formula and write equations for the reactions by which the sodium acetate is produced.

## 8.2 Fats

Fats in Nature. Physical Properties of Fats. Fats widely occur in nature. Together with carbohydrates and proteins, they are contained in all plants and animals, and make essential component of our nutrition.

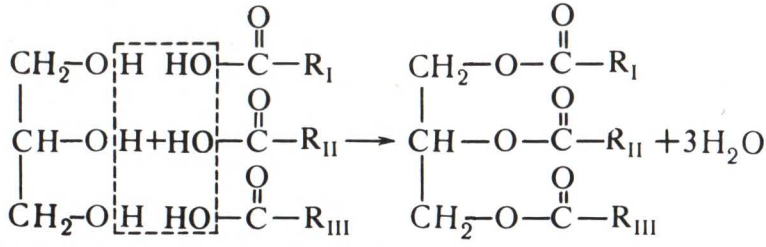
Animal fats are, as a rule, solids. Vegetable fats are more often liquid and called oils. Animal fats can however also be liquid, e.g. cod-liver oil, white vegetable fats can be solid, e.g. coconut oil.

Fats are lighter than water. They are insoluble in it but are readily dissolved in organic solvents (e.g. dichloroethane, benzol).

Structure of Fats. The structure of fats was established by the French chemists Chevreul and Berthelot. In the early 19th century, Chevreul heated a mixture of fats with water in the presence of an alkali and established that fats combine with water and decompose into glycerol and carboxylic acids, such as stearic, oleic, and others. Berthelot discovered the reverse reaction in 1854. He heated a mixture of glycerol and certain carboxylic acids to prepare substances similar to fats.

Chevreul probably hydrolyzed an ester, while Berthelot realized an esterification process, i.e. synthesized an ester. We can now conclude that fats are esters of the trihydric alcohol, glycerol, and carboxylic acids.

These esters are usually formed not by an individual acid but by various acids. The process can therefore be expressed as follows:



In most cases, fats are formed from saturated and unsaturated carboxylic acids with many carbon atoms, mainly palmitic $C_{15}H_{31}$—COOH, stearic $C_{17}H_{35}$—COOH, oleic $C_{17}H_{33}$—COOH, and linoleic $C_{17}H_{31}$—COOH acids. Lower members of carboxylic acids are found less often in fats. These are, for example, butyric acid $C_3H_7$—COOH (in butter), and caproic acid $C_5H_{11}$—COOH.

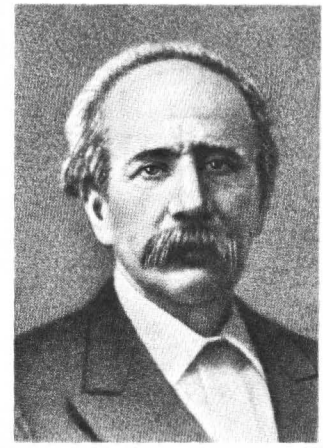
It is interesting to note that natural fats are usually formed by acids having unbranched carbon chains with even number of carbon atoms.

Fats formed predominantly by saturated acids are solids (beef and mutton suet, and tallow). The melting points of fats decrease as their content of unsaturated acids increases, and they melt more readily (lard, butter). Liquid fats are mainly formed by unsaturated acids (sunflower and cotton-seed oil).

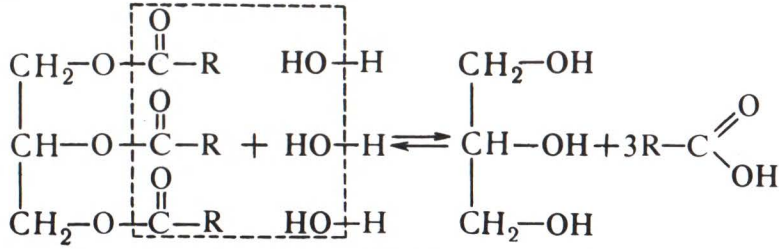
Chemical Properties. The chemical properties of fats result from their being esters. The most characteristic reaction of fats is therefore hydrolysis.

Marcelin Pierre Eugene BERTHELOT (1827–1907)

Berthelot was an outstanding French organic chemist. He synthesized many organic compounds, including methane (by the reaction between hydrogen sulphide and carbon disulphide), acetylene (by combining carbon and hydrogen directly), benzene (from acetylene), ethyl alcohol (from ethylene), formic acid (the salt of the acid, by the interaction of potassium hydroxide with carbon dioxide), fats (by heating glycerol and the corresponding carboxylic acids). He synthesized ethylene, and then ethane, by adding hydrogen to acetylene. Berthelot's contributions to thermal chemistry, agriculture, and chemistry were also important.



The hydrolysis of fats (like other esters) is reversible. This can be expressed as follows:



What conditions, in your opinion, will shift the equilibrium towards the formation of glycerol and the carboxylic acids?

Assimilation of fats from food is associated with their hydrolysis. Under the action of enzymes secreted by the pancreas and the stomach, the fats are hydrolyzed in the small intestine into glycerol and acids. The products of the hydrolysis are then absorbed in the intestine and form fats again. These newly formed fats meet the specific requirements of a particular animal. During cell metabolism, fats are hydrolyzed again and then oxidized gradually to carbon dioxide and water. The exothermic reaction of oxidation yields the energy, which is necessary for a living organism.

Industrial Hydrolysis of Fats. The hydrolysis reaction is used in industry for the manufacture of glycerol, carboxylic acids, and soaps.

Glycerol and acids are prepared by heating fat and water in an autoclave.

Soaps are manufactured by heating acids with a soda solution (write down the reaction equation). In order to isolate the soap formed, sodium chloride is added to the solution. The soap then floats to the surface in the form of a dense mass from which hard soaps are manufactured.

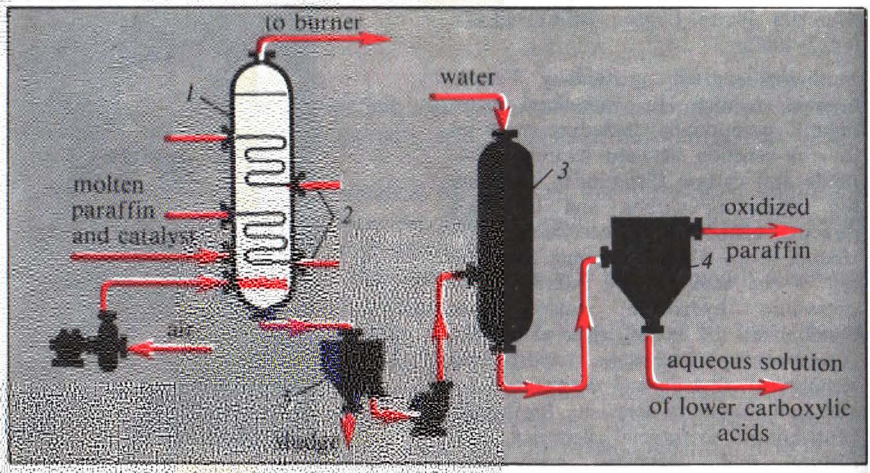



Fig. 48. Industrial manufacture of carboxylic acids by oxidation of paraffins: 1 – oxidation column; 2 – cooler; 3 – scrubber; 4 – separator; 5 – settling vessel

Toilet soaps are prepared by drying hard soap, mixing it with dyes and scents, and pressing them into cakes. Toilet soaps can also be obtained directly from the carboxylic acids.

**Hydrogenation of Fats.** Solid fats are mostly used in the manufacture of soaps and some other products. However, fats are also valuable as food. Thus, it is more reasonable to use the cheaper vegetable oils for industrial purposes after converting them into solids.

Remember that liquid oils differ from solid fats by their degree of saturation, i. e. by the presence of double bonds in their hydrocarbon radicals. This means that liquid oils can be converted into solid fats by hydrogenation, in the same way as liquid unsaturated acids can be solidified.

The hydrogen is passed under pressure through a hot oil mixed with a finely divided catalyst (nickel and/or copper). The hydrogen is attached to the double bonds of the hydrocarbon radicals and the oil is thus converted into a solid fat (see Appendix, Fig. II):

$$\begin{array}{l} CH_2-O-CO-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 \\ | \\ CH-O-CO-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 + 3H_2 \longrightarrow \\ | \\ CH_2-O-CO-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 \end{array}$$

$$\longrightarrow \begin{array}{l} CH_2-O-CO-(CH_2)_{16}-CH_3 \\ | \\ CH-O-CO-(CH_2)_{16}-CH_3 \\ | \\ CH_2-O-CO-(CH_2)_{16}-CH_3 \end{array}$$

Industrial hydrogenation is carried out in several autoclaves that are connected in series. As the fat moves through the system of autoclaves, it is hydrogenated more and more, until the initial liquid oil turns into a mass with the consistency of lard. The catalyst is separated from the fat by filtration. Hydrogenated fat is suitable for the manufacture of soaps; some sorts of oil are processed into cooking fats, such as margarine.

**Synthetic Detergents.** Fats are necessary for the manufacture of soaps, but we have already mentioned that fats are used as foods. In order to save them, soaps are produced from materials other than food.

Remember that soaps contain the salts of carboxylic acids. These are now produced industrially by the oxidation of the hydrocarbons contained in paraffin wax. The process is carried out in columns where air is blown at a temperature of 120 °C through a molten mixture of hydrocarbons in the presence of manganese compounds as catalysts (Fig. 48). The hydrocarbon molecules are cracked and their terminal groups are oxidized to carboxylic acids, for example:

$$2CH_3{-}(CH_2)_{14}{-}CH_2{-}CH_2{-}(CH_2)_{14}CH_3 + 5O_2 \longrightarrow$$

$$\longrightarrow 4CH_3{-}(CH_2)_{14}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + 2H_2O$$

A mixture of various acids and other acid-containing compounds is formed, which is then separated. The salts are finally obtained by neutralization, which when mixed with fillers are used for the manufacture of toilet and laundry soaps.

Soaps obtained from synthetic acids are chemically similar to common soaps. Therefore, they have the same disadvantages as natural soaps. Their washing properties, for example, are impaired in hard water. Detergents of other types are therefore now produced.

The salt of the acid esters of higher alcohols and sulphuric acid is one of such synthetic detergents. It is prepared as follows:

$$R{-}CH_2{-}OH + HO{-}SO_2{-}OH \rightarrow R{-}CH_2{-}O{-}SO_2{-}OH + H_2O$$

Acid ester of alcohol and sulphuric acid

$$R{-}CH_2{-}O{-}SO_2{-}OH + NaOH \rightarrow R{-}CH_2{-}O{-}SO_2{-}ONa + H_2O$$

Sodium salt of ester

These salts are similar in structure to those contained in common soap: they also contain a long water-insoluble hydrocarbon chain and a soluble functional group. They are therefore surface-active substances, like soaps, and have good washing properties. As distinct from common soaps, they do not lose their washing properties in hard water, because the formed calcium and magnesium salts are soluble, and the surface-active substance therefore remains in solution and does not precipitate.

Large quantities of synthetic detergents are manufactured in the form of powders. But many of them are not destroyed in use and thus contaminate the environment. Therefore, scientists are now working to find new detergents that will be destroyed after they have been used by some microorganisms.

?

1. How was the structure of fats established? Write down the equations of the reactions Chevreul and Berthelot discovered.

△

2. What is the difference between the structure of solid and liquid fats?
3. Write down the structural formula of the esters formed by glycerol and butyric, oleic, and stearic acids.
4. Once the oleic acid is known to have *cis*-structure, explain why the fats formed by this acid are liquids.
5. How can linseed oil be differentiated chemically from lubricating oil obtained from petroleum?
6. Write down the equation for the oxidation of triacontane $C_{30}H_{62}$ assuming that a monocarboxylic saturated acid with 15 carbon atoms is formed.
7. The consumption of soap increases considerably if hard water is used for laundry. Explain.
8. Synthetic detergents form froth in both soft and hard water. Explain.

■

9. Carry out the following experiments at home: (a) clean an oil-spotted fabric with petrol, (b) compare the foaming of common soap and synthetic detergent powder in hard water, (c) soften water by adding soda and by boiling; compare the results.

# 9 Carbohydrates

Carbohydrates occur widely in nature and are very important to man. Some carbohydrates, such as starch, are necessary for nutrition of man, while others (e.g. cellulose) are used to manufacture textiles, paper, artificial fibres, etc.

The name 'carbohydrates' came from the early observation that most compounds of this group had the empirical formulas $C_n(H_2O)_m$, suggesting that they were hydrates of carbon. Hence, carbohydrates. The idea was later proved incorrect but the group name has survived.

One of the simplest carbohydrates is glucose.

## 9.1 Glucose

Physical Properties and Occurrence in Nature Glucose is a colourless crystalline substance, readily soluble in water. It tastes sweet, hence the name (from Greek *gleukos*, must). Glucose occurs in almost every part of a plant: fruit, roots, leaves, and flowers. Its content is especially high in the juice of grapes, in ripe fruits and berries. Glucose is contained in animal tissues as well. Human blood contains about 0.1 per cent of glucose.

Structure of Glucose. The formula of glucose is $C_6H_{12}O_6$. Let us consider the structure of this carbohydrate.

Since the molecule of glucose contains oxygen, it is natural to ask whether glucose contains any of the functional groups we know.

Since there are many oxygen atoms in the glucose molecule, we might think that glucose could be a polyhydric alcohol. If a glucose solution is added to a freshly precipitated copper(II) hydroxide, a bright blue solution is formed just as in the case of glycerol. This experiment proves that glucose is a polyhydric alcohol.

But now we ask how many hydroxyl groups are contained in the molecule of glucose?

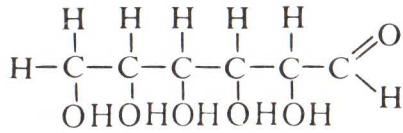
One ester of glucose is known whose molecule contains five residues of acetic acid. It follows that glucose has five hydroxyl groups. This fact accounts for the good solubility of glucose in water and its sweet taste.

What remains is to find out the character of the sixth oxygen atom. If a glucose solution is heated with an ammoniacal solution of silver(I) oxide, the specific "silver mirror" appears. This indicates that the sixth oxygen atom belongs to the aldehyde group.

And finally, we must know the structure of the carbon chain in the glucose

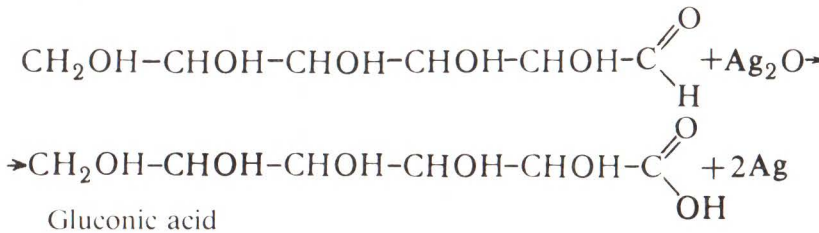
molecule. Since all the oxygen atoms are contained in the functional groups, all the carbon atoms must be connected directly with one another. It has been established that the carbon chain is straight, not branched. Finally, we know that the aldehyde group may be found only at the end of an unbranched carbon chain (why?) and that the hydroxyl groups may only be stable when they are attached to different carbon atoms.

From all that we know now about the chemical structure of glucose, we can write its formula as follows:



The formula shows that glucose is both an aldehyde and a polyhydric alcohol.

Chemical Properties. The structure of glucose shows that this substance has a dual chemical function. Being a polyhydric alcohol, glucose forms esters, and being an aldehyde, it can be oxidized. Remember the action of an ammoniacal solution of silver(I) oxide on glucose. Now we can write an equation for this reaction:



Gluconic acid

Some other products of oxidation are formed in this reaction. Copper(II) hydroxide can also oxidize the aldehyde group of glucose. If a glucose solution is added to a small amount of freshly precipitated copper(II) hydroxide, and the mixture is heated, the red copper(I) oxide is formed. The equation of this reaction is similar to that for the oxidation of aldehydes.

The aldehyde group of glucose can be reduced to give a hexahydric alcohol:

$$CH_2OH—CHOH—CHOH—CHOH—CHOH—CH_2OH$$

An important property of glucose is its fermentation by enzymes, produced by microorganisms, which act as an organic catalyst.

There are several types of fermentation. One of them is *alcoholic fermentation*. We have already discussed it partly when we studied methods for preparing ethyl alcohol. The chemistry of alcoholic fermentation, which is catalyzed by yeast, is very complicated. It can be expressed by the overall expression

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Lactic acid bacteria (lactobacteria) cause *lactic fermentation* of glucose, which

can be expressed like this:

$$C_6H_{12}O_6 \longrightarrow 2CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$$

Lactic acid

The lactic acid is also a compound with two chemical functional groups, because it combines the properties of alcohol and a carboxylic acid.

The lactic acid is formed in sour milk. Its presence in milk can be detected by litmus.

The lactic fermentation is very important for manufacturing diary products, such as yoghurt, curds, cheese, sour cream, etc. The lactic acid is formed in sour cabbage and animal feed (silo), in which the acid acts as a preservative. The lactic acid formed in compressed silo mass creates an acid medium thus preventing putrefaction of proteins or other undesirable chemical processes.

Uses of Glucose. Glucose is a valuable nutrient substance. From the course in biology we know that starch is converted in the alimentary tract into glucose, which is carried by our blood to the tissues and cells of the body, where glucose is oxidized to produce the energy needed for the body. The final products of this oxidation are carbon dioxide and water

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Since this oxidation proceeds in steps, the energy is also liberated stepwise. The energy is partly liberated as heat, but the most of it is consumed in the synthesis of adenosinetriphosphoric acid (ATP) which is an accumulator of energy in the body. The energy liberated by ATP during subsequent decomposition, is used by the body to perform work (muscles contraction, secretion, synthesis of substances, etc.).

Glucose is easily assimilated by the body and is therefore used in medicine as a tonic. The sweet taste of glucose accounts for its use as a confectionary. Being a reducing agent, it is used to manufacture mirrors and various decorations for Christmas tree. Glucose is used in the textile industry for trimming fabrics.

Glucose is obtained in industry from more complicated carbohydrates, mostly starch, by heating it with water in the presence of catalysts (mineral acids).

Fructose (Isomer of Glucose). Some other carbohydrates that are isomers of glucose and have the same formula $C_6H_{12}O_6$ are known. Fructose is one of them:

$$CH_2OH-CHOH-CHOH-CHOH-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2OH$$

The structure shows that fructose is a keto-alcohol. It is contained in sweet fruits; equal quantities of fructose and glucose constitute the main part of honey.

Fructose is sweeter than glucose and common sugar.

? 1. Explain why monohydric alcohols and monocarboxylic acids that like glucose contain six carbon atoms in their molecules are insoluble, while glucose is readily soluble in water?

△ 2. Which experiments can be used to establish the structure of glucose? Describe them.

3. Write down the equations for (a) the oxidation of glucose by copper(II) hydroxide, (b) the reduction of glucose into hexahydric alcohol.

4. How many grams of calcium carbonate will be obtained by the absorption of the carbon dioxide, liberated during the fermentation of 1 mole of glucose, in lime water?

5. What volume of carbon dioxide is formed after the complete oxidation of 1 mole of glucose?

6. Using one reagent, identify (a) glycerol, (b) aldehyde, (c) acetic acid, and (d) glucose. Give the reaction equations.

7. Remembering that the lactic acid has the properties of both alcohol and acid, write down the equations for its reaction with (a) sodium, and (b) sodium hydroxide.

## 9.2 Sucrose

**Physical Properties and Occurrence in Nature.** Sucrose is well known to everyone as common sugar. It is a sweet crystalline substance readily soluble in water. The melting point of sucrose is 160 °C. As the molten sugar solidifies, an amorphous clear mass is obtained. This is known as caramel.

Sucrose is contained in many plants, for example, in birch sap, maple syrup, carrots, melon, etc. Sugar beet and sugar cane contain large quantities of sucrose. These plants are used for obtaining sucrose.

**Structure and Chemical Properties.** The molecular formula of sucrose is $C_{12}H_{22}O_{11}$. Its structure is more complicated than that of glucose. Let us first find out if it contains the functional groups that we discovered in glucose.

The presence of hydroxyl groups in the sucrose molecule can be easily detected by its reaction with metal hydroxides. If a solution of sucrose is added to copper(II) hydroxide, a bright blue solution of copper saccharate is formed (remember copper glycerate).

No aldehyde group can be detected in sucrose: when heated with ammoniacal solution of silver oxide the "silver mirror" reaction does not occur, nor does sucrose form red copper(I) oxide when heated with copper(II) hydroxide. This indicates that, unlike glucose, sucrose is not an aldehyde.

An important conclusion about the structure of sucrose may be made by studying its reaction with water. Boil a sugar solution with a few drops of hydrochloric or sulphuric acid. Neutralize the acid with an alkali and heat the solution with copper(II) hydroxide: a red precipitate appears. This shows that when the sucrose was boiled, molecules with aldehyde groups appeared in solution. They reduced copper(II) hydroxide to copper(I) oxide. A study of this reaction shows that sucrose is hydrolyzed by the catalytic action of acid to give glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

It can be concluded that the sucrose molecule consists of combined glucose and fructose residues.

Isomers of Sucrose. Maltose and lactose should be mentioned among the isomers of sucrose having the molecular formula $C_{12}H_{22}O_{11}$.

Maltose is obtained from starch by the action of malt. It is therefore called malt sugar. It is hydrolyzed to give glucose

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow 2\underset{\text{Glucose}}{C_6H_{12}O_6}$$

Lactose, or milk sugar, occurs only in milk and is very nutritious. When hydrolyzed, lactose decomposes into glucose and galactose (an isomer of glucose and fructose).

1. How can solutions of glucose and sucrose be differentiated?
2. How can it be shown whether or not sucrose is hydrolyzed in a cup of sweet tea?
3. How much glucose (a) in moles, (b) in grams, can be prepared by hydrolyzing 5 moles of sucrose?
4. If lime milk (calcium hydroxide suspended in water) is added to a sucrose solution and the mixture shaken, the precipitate is dissolved. Explain.

5. Perform the following experiments at home: (a) observe the changes occurring in sugar when heated; (b) determine the solubility of sugar in water at room temperature.

## 9.3 Starch

Physical Properties and Occurrence in Nature. Starch is a white powder insoluble in water. It forms a colloidal solution in hot water (starch size).

Being the product of the assimilation of carbon dioxide by the green (chlorophyll containing) cells of plants, starch occurs widely in nature. Potato tubers contain about 20 per cent of starch, wheat and maize grains contain about 70 and rice about 80 per cent of starch.

Starch is one of the most important constituents of the human diet.

Structure of Starch. Starch $(C_6H_{10}O_5)_n$ is a natural polymer. From biology we know that starch is formed in plants by photosynthesis as they absorb the energy of sunlight. Glucose is first formed from carbon dioxide and water (try to remember the main processes involved):

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Glucose is then converted into starch:

$$nC_6H_{12}O_6 \rightarrow (C_6H_{10}O_5)_n + nH_2O$$

As in all other high-molecular substances, the macromolecules of starch differ in size because they contain different numbers of the repeat units $C_6H_{10}O_5$. The number of units varies from several hundreds to several thousands. The subscript $n$ in the starch formula therefore indicates only an average number.

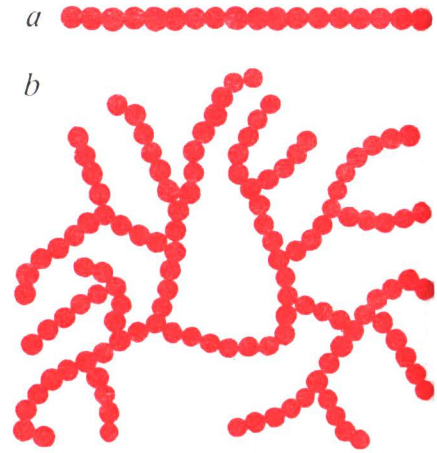



Fig. 49. Structure of starch molecules

The molecular weight of starch is thus not definite and can only be regarded as an average molecular weight.

Unlike many other high-molecular compounds, starch molecules differ not only in the numbers of repeat units but in their structures as well. In addition to linear molecules (Fig. 49*a*), whose average molecular weight is several hundreds of thousands, there are starch molecules with branched structure (Fig. 49*b*) whose molecular weights may be several millions.

Chemical Properties. We already know one property of starch. This is its ability to give a blue colour to iodine solution. This colour can be easily observed if a drop of iodine solution is placed on a piece of potato or a slice of wheat bread.

Are the properties of carbohydrates inherent in starch as well?

Heat an aqueous solution of starch with copper(II) hydroxide: copper(I) oxide is not formed. This shows that starch does not have the reducing properties of glucose.

Now let us test starch for a property of sucrose: the ability to be hydrolyzed. Boil a starch solution with a small quantity of sulphuric acid, neutralize the solution, and try to carry out the reaction with copper(II) hydroxide. The characteristic precipitate of copper(I) oxide is formed, indicating that starch is hydrolyzed when heated in water in the presence of an acid. The reaction also yields a substance that reduces copper(II) hydroxide to copper(I) oxide.

It has been established that the decomposition of starch molecules by water takes place in steps. Intermediate products with smaller molecular weights are first formed. These are dextrins. Maltose, the isomer of sucrose, is formed next. The final product of the hydrolysis is glucose.

The formation of glucose can be shown schematically as follows:

$$\cdots\!-\!C_6H_{10}O_5\!-\!C_6H_{10}O_5\!-\!C_6H_{10}O_5\!-\!C_6H_{10}O_5-\cdots \longrightarrow n\,C_6H_{12}O_6$$
$$\quad\;\; H\!-\!OH \quad\; H\!-\!OH \quad\; H\!-\!OH \quad\; H\!-\!OH$$

or in a shorter way

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$

The conversion of starch into glucose by the catalytic action of sulphuric acid was discovered in 1811 by the Russian investigator Kirchhoff. His discovery is still used for the manufacture of glucose in our days.

Uses of Starch and Its Manufacture. Starch is the main carbohydrate constituent of human food. Like the fats, it is first hydrolyzed in the human body. The process begins in the mouth when the food is mixed with the saliva as we chew. The hydrolysis is continued in the stomach and the intestine. The glucose formed is absorbed into the intestine and delivered to the blood, then to the liver, and then to all the other tissues of the body.

The intermediate products of starch hydrolysis (dextrins) are more easily assimilated by the body than starch itself, because their molecules are smaller and more soluble in water. Cooking often involves the conversion of starch into dextrins. Starch is partially hydrolyzed when we boil potatoes or bake bread. The formation of glue-like dextrins accounts for the appearance of crust on the bread and roast potatoes.

Starch is used not only as food. Glucose and syrups are produced from starch in food industry.

Glucose is prepared by heating starch with dilute sulphuric acid for a few hours. As soon as the hydrolysis is over, the acid is neutralized with chalk, the precipitated calcium sulphate is filtered out and the solution is evaporated. Crystalline glucose precipitates when the solution is cooled.

If the hydrolysis is not completed, a sweet mass, a mixture of dextrins and glucose, is formed. This is called theacle, or syrup. It is used for the manufacture of sweets or candy. They remain soft for a longer time and their sweet taste is better than that of products prepared with pure sucrose.

The dextrins prepared from starch are used as glues. Starch itself is used for laundry. When pressed by a hot iron, starch is converted into dextrins, which glue together the fibres of the textile to form a hard film which prevents linen from soiling quickly.

Starch (in the form of potato or cereals) is used in the manufacture of ethyl alcohol. It is first hydrolyzed by the enzymes contained in malt, and the hydrolyzed product is then fermented in the presence of yeast. The ethyl alcohol intended for industrial uses (synthesis of rubber) is synthesized from ethylene or obtained by hydrolysis of another carbohydrate, cellulose.

Starch is mostly prepared from potatoes, which are crushed and washed with water on a gauze. The starch grains released from potato tubers pass through the gauze with water and precipitate. The precipitated starch is then separated from the supernatant, washed thoroughly and dried.

? △

1. Characterize starch as a high-molecular substance.
2. Describe the process of photosynthesis of starch in plants using your knowledge of general biology.
3. Assume that starch is completely hydrolyzed to glucose. Decide if the weight of the produced glucose is smaller or higher than the starting weight of starch. Explain your answer.
4. How can the adhesive properties of boiled potato be explained?

5. Write down the equations of reactions for the preparation of ethyl alcohol from starch:

$$(C_6H_{10}O_5)_n \xrightarrow{(1)} C_6H_{12}O_6 \xrightarrow{(2)} C_2H_5OH$$

What sort of reactions are (1) and (2)?

6. The juice of an unripe apple reacts with iodine. The juice of a ripe apple reduces an ammoniacal solution of silver oxide. Explain these reactions.

■ 7. Carry out the following experiments at home: (a) dilute 10 times a small portion of an iodine tincture and use this aqueous solution to test cooked potato, wheat bread, crushed rice, chalk, etc., whether they contain starch; (b) prepare a starch size, add iodine and observe the change in colour as the solution is heated and then cooled; (c) starch a piece of fabric.

## 9.4 Cellulose

Occurrence in Nature. Physical Properties. Cellulose is found mainly in the structural parts of plants. It gives plants their strength and elasticity and makes up the plant's "skeleton". It is contained in the coats of cells, hence the name.

Cotton fibres contain up to 98 per cent of cellulose; flax and hemp fibres also consist mainly of cellulose. Wood contains about 50 per cent of cellulose. Paper and cotton fabrics are products from cellulose. Especially pure specimens of cellulose are cotton wool, which is prepared from purified cotton, and filter (blotting) paper.

Cellulose prepared from natural materials is a solid fibrous substance insoluble in water or the common organic solvents.

Structure of Cellulose. Like starch, cellulose is a natural polymer. It has been found that the structural (repeat) units of starch and cellulose are the same, and hence their formula is also the same: $(C_6H_{10}O_5)_n$. The question now is why the properties of these two substances are so different?

It can be supposed that the macromolecules of starch and cellulose differ in the number of repeat units or in their spatial structure. In fact, the value of $n$ is usually higher in cellulose with average molecular weight of several millions.

But the main difference between starch and cellulose is in the structure of their molecules. The molecules of starch are linear and branched, while cellulose has only linear molecules* $-C_6H_{10}O_5-C_6H_{10}O_5-C_6H_{10}O_5-$ $-C_6H_{10}O_5-\ldots$ This explains why cellulose forms fibrous materials, such as flax, cotton, hemp, etc. Macromolecules in natural fibres are arranged in one direction, i.e. they are oriented along the axis of the fibre (Fig. 50). Numerous hydrogen bonds that arise between the hydroxyl groups of the macromolecules account for the high strength of these fibres. Cotton, flax and other fibres are

* The difference between the properties of starch and cellulose depends also on a slight difference in the structure of their repeat units.

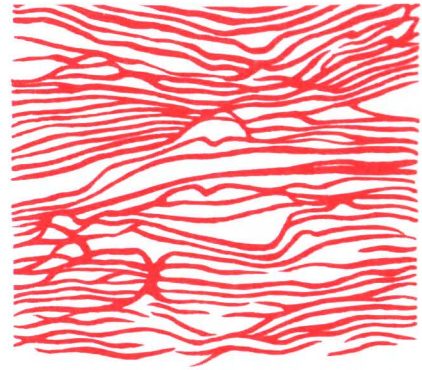


Fig. 50. Orientation of cellulose molecules

spun into long threads. The cellulose of wood cannot be used for spinning thread, because its macromolecules (although linear) are arranged at random (not oriented in one direction).

The difference in the structure of molecules of starch and cellulose might appear insignificant. But the properties of these two materials differ so greatly that starch can be used as a food, while cellulose cannot.

Chemical Properties. From everyday experience we know that cellulose is combustible. When wood is heated without air, cellulose is thermally decomposed to give volatile organic products, water, and charcoal. The decomposition products of wood are methyl alcohol, acetic acid, and acetone.

Since the macromolecules of cellulose consist of units that are very similar to those forming starch, one would expect that cellulose can be hydrolyzed, and that the hydrolysis product should be glucose, like in hydrolysis of starch.

Grind a piece of filter paper wetted with concentrated sulphuric acid in a porcelain mortar, dilute the mass with water, neutralize with alkali, and (as in the case with starch) try the action of copper(II) hydroxide on it: copper(I) oxide is produced. This indicates that cellulose was hydrolyzed in our experiment. As in the case with starch, this process is stepwise, the final product of the hydrolysis being glucose.

The overall equation of this process can be expressed as follows:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$

The structural unit of cellulose $C_6H_{10}O_5$ (like the repeat unit of starch) contains three hydroxyl groups. In structural formulas they are sometimes shown as follows:

$$\left[C_6H_7O_2\begin{matrix}OH\\-OH\\OH\end{matrix}\right]_n \quad \text{or} \quad \left[C_6H_7O_2(OH)_3\right]_n$$

Ethers and esters can be formed by cellulose due to the presence of these groups.

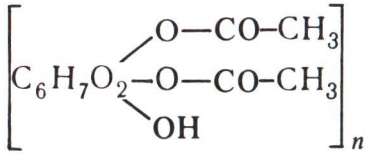
The nitric esters of cellulose are very important. They are obtained by the

action of nitric acid on cellulose in the presence of sulphuric acid. Depending on the concentration of the nitric acid and on other conditions, one, two, or three hydroxyl groups of each repeat unit of cellulose are involved in esterification:

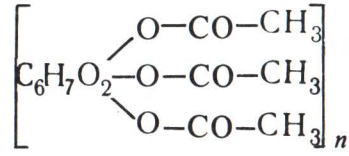
$$[C_6H_7O_2(OH)_3]_n + 3nHNO_3 \rightarrow [C_6H_7O_2(ONO_2)_3]_n + 3nH_2O$$

The property common to all the cellulose nitrates (nitrocellulose) is their extraordinary flammability. Cellulose nitrates are powerful explosives and used to manufacture gunpowder.

Cellulose diacetate and triacetate are also very important:



Cellulose diacetate



Cellulose triacetate

They look like cellulose and are used to make acetate fibres.

Uses of Cellulose. It is used by man in a variety of ways. Because of its mechanical strength we use it (wood) for building and furniture. Cotton, flax and hemp are used in the manufacture of threads, fabrics, ropes. When purified, cellulose is used to make paper. Cellulose is hydrolyzed to give glucose which is then fermented to prepare alcohol. The esters of cellulose are used to make varnishes, films, medicinal collodions, man-made fibres, etc.

Preparing Acetate Fibres. Man has used natural fibres for a long time to make clothes and various domestic articles. These materials can be divided into two major groups, one of them including materials of vegetable origin, such as cotton, flax, and the others including materials of animal origin, such as wool, and silk. Vegetable fibres consist of cellulose while animal fibres are made up of proteins.

However, the growing demands of an increasing population could not be met by natural fibre sources alone and so it became necessary to create chemical fibres.

Artificial fibres can be obtained chemically by two major methods. Since fibres have an orderly arrangement of linear macromolecules, natural polymers with disordered structures can be processed so that the macromolecules could be arranged in it in the oriented order. The other way is to produce a synthetic polymer whose macromolecules are then arranged in it as required.

Man-made fibres are now manufactured by both methods. All man-made fibres can thus be divided into two major groups: natural polymers and synthetic polymers. Natural polymer fibres are produced by the appropriate treatment of natural polymers, and synthetic polymer fibres are manufactured from synthesized materials. However, they are all called chemical fibres because they are obtained using chemical processes (Fig. 51).

The starting material used for the manufacture of natural polymer fibres is cellulose isolated from wood or cotton.

In order to arrange the linear molecules along the axis of the fibre, they must first be separated, made movable and capable of being rearranged. This can be done by melting or dissolving the polymer. It is impossible to melt cellulose

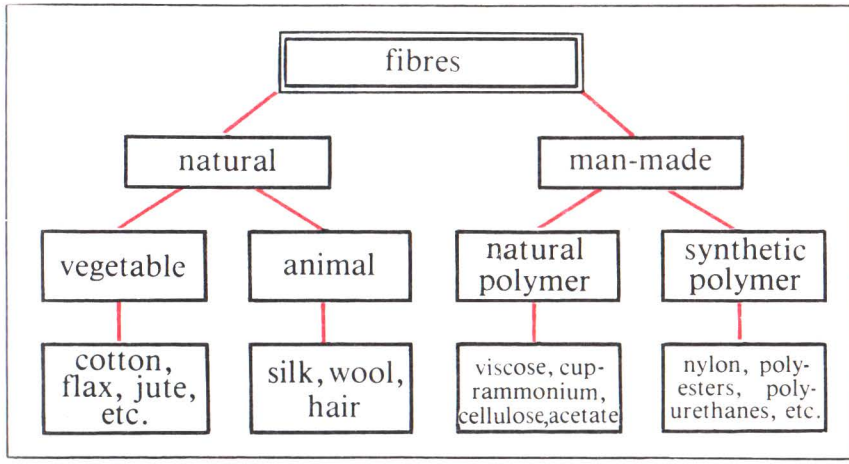



Fig. 51. Classification of fibres

because it decomposes when heated. It has therefore to be dissolved. Cellulose is treated with acetic acid anhydride* in the presence of sulphuric acid. (Acetic acid anhydride is a stronger esterifying agent than acetic acid.)

The product of esterification is cellulose triacetate. It is dissolved in a mixture of dichloromethane $CH_2Cl_2$ and ethyl alcohol to give a viscous solution in which the molecules are movable and can be arranged in the wanted order.

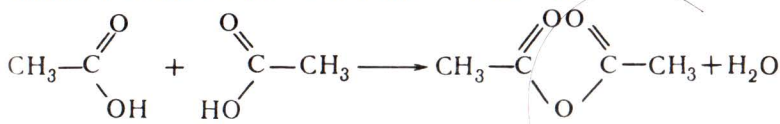
Fibres are made by forming the solution through a die (spinneret), which is a cap with small perforations (Fig. 52). The fine jets of the viscous liquid are extruded into a 3-metre shaft through which hot air is passed.

The solvent is evaporated and the cellulose triacetate sets into fine long fibres. As the macromolecules pass through the holes in the die, they are arranged lengthwise, just like legs of timbers arrange themselves in a stream as they float down a narrow river. As they are processed further the molecules become even more ordered. This makes the fibres very strong.

Man-made fibres are often used not in the form of long threads (as in silk) but as staples, which are short untwisted fibres a few centimetres long. Staples can be used for spinning together with other fibres, such as wool.

The strength of acetate fibres is less affected by damp than viscous rayon. Its heat conductivity is lower and garments made of acetate fibre are warmer. Acetate fibres are soft to touch, do not shrink very much after laundry, and fabric made from them has a pleasant lustre. Thus acetate fibre is a valuable textile. However, acetate fibre is inferior to cotton with respect to hygiene. Since

* Acetic acid anhydride can be regarded as the product of the elimination of water from two molecules of acetic acid:



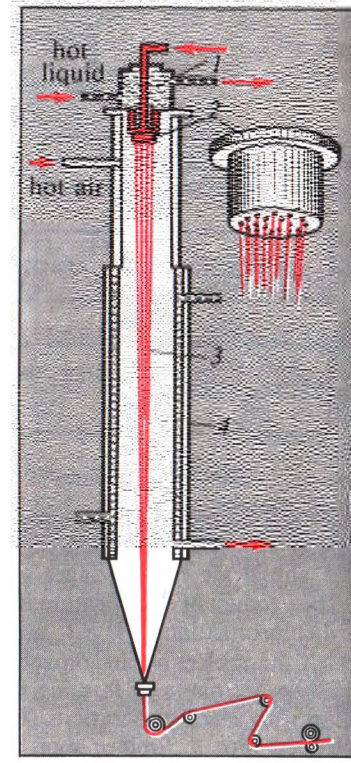



Fig. 52. Manufacture of acetate fibre:
*1* – spinning head; *2* – spinneret; *3* – fibres; *4* – shaft

most of the hydroxyl groups are esterified, acetate fibre molecules are less able to establish hydrogen bonds with water molecules and the fibre therefore absorbs moisture with a greater difficulty.

?

1. What is common and what are the differences between the structures of starch and cellulose?

△

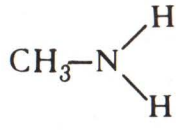
2. How many repeat units ($C_6H_{10}O_5$) are contained in the cellulose molecule (what is the value of $n$ in the molecular formula) of (a) a flax fibre ($M_r = 5\,900\,000$) (b) a cotton fibre ($M_r = 1\,750\,000$)?
3. Why can fibres be obtained from cellulose and not from starch?
4. The molecules of rubber and cellulose are linear. Why do the properties of rubber and cellulose fibres differ so much? (Rubber is not as strong as the fibres, while the fibres are not as elastic as rubber.)
5. What chemical property is common to sucrose, starch, and cellulose? Give equations to illustrate your answer.
6. Write down the equations for the reactions by which (a) cellulose dinitrate and (b) cellulose triacetate are obtained.
7. Write down the equations for the reactions by which ethyl alcohol can be prepared from cellulose.
8. What are the main stages in the manufacture of acetate fibre? How are fibres molded?

# 10 Amines. Amino Acids. Proteins.

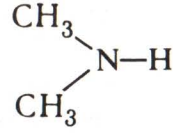
When we studied the hydrocarbons and oxygen-containing organic substances, we mentioned compounds that contained nitrogen. These compounds are very important for the economy. They are especially important for the living world, because biologically important compounds such as proteins and nucleic acids also contain nitrogen. We shall now consider some classes of nitrogen-containing organic compounds.

## 10.1 Amines

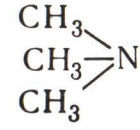
**Structure and Properties.** Nitrogen can be contained in organic compounds not only as the residue of nitric acid (remember nitrobenzene $C_6H_5NO_2$ and cellulose trinitrate $[C_6H_7O_2(ONO_2)_3]_n$), but also in other forms. Many organic compounds are known in which nitrogen is contained as the derivative of ammonia:



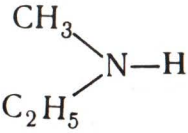
Methylamine



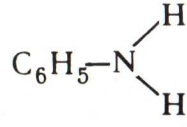
Dimethylamine



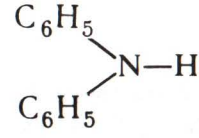
Trimethylamine



Methylethylamine



Phenylamine (aniline)



Diphenylamine

All these compounds are called amines.

● Amines are the derivatives of ammonia in which one or several hydrogen atoms are replaced by hydrocarbon groups.

We shall mostly study amines containing a univalent *amino group* $—NH_2$ as the functional group. Figure 53 shows a model of the simplest amine molecule.

The resemblance between ammonia and amines is not only formal. These substances have some properties in common.

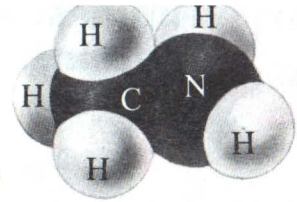



Fig. 53. A model of a molecule of methylamine

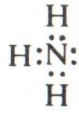
The lower members of the saturated amine series are gases and smell of ammonia. They were formerly mistaken for ammonia, but it was later discovered that they burn in the air, while ammonia does not (remember the conditions under which ammonia burns):

$$4CH_3—NH_2 + 9O_2 \rightarrow 4CO_2 + 10H_2O + 2N_2$$

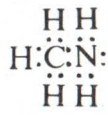
If an amine is dissolved in water, the solution will be alkaline (as tested by litmus), as in the case of ammonia. Amines are therefore characterized by the basic properties.

The similarity between the properties of the amines and ammonia is explained by their electron structure.

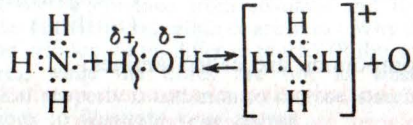
Three of the five valency electrons of the nitrogen atom in the ammonia molecule are involved in the formation of covalent bonds with hydrogen atoms, while one electron pair remains free:

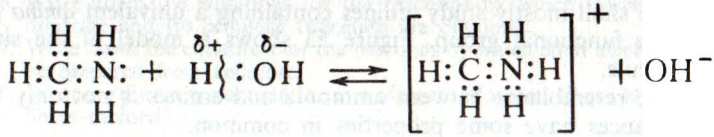


The electron structure of the amines is similar to that of ammonia. The nitrogen of amine also has an unshared electron pair:



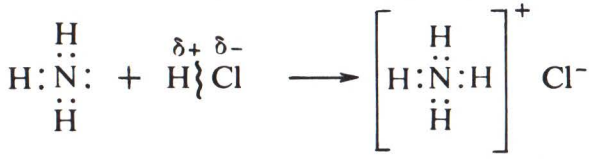
When amines react with water they attach a proton at the free electron pair. This results in the accumulation of the hydroxide ions and their solutions are therefore alkaline:



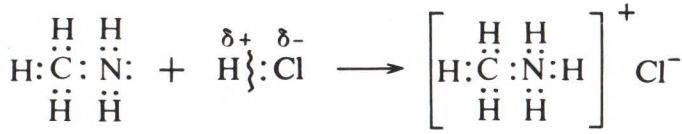


When we studied inorganic chemistry, we defined the substances whose metal atoms are connected with one or more hydroxyl groups as bases. But the concept of a base is wider. The properties of bases are opposite to those of acids. Therefore the elimination of protons is characteristic of acids, while bases, on the contrary, attach protons in chemical reactions. It follows, therefore, that not only the products of reactions of ammonia and amines with water, but also ammonia and amines themselves are bases. The amines are also called *organic bases*.

Like bases, amines react with acids to give salts. This reaction is similar to the known reactions of ammonia and also involves the attachment of a proton:



Ammonium chloride



Methylammonium chloride

But these substances have also differences. Amines are the derivatives of the saturated hydrocarbons and are stronger bases than ammonia. Since the amines only differ from ammonia by the presence of hydrocarbon radicals, the radicals probably affect the nitrogen atom.

We know that the hydrocarbon radical affects the displacement of the electrons in the covalent bond. Under the influence of the $-CH_3$ radical, the electron cloud of the C—N bond is displaced in an amine towards the nitrogen, and the electron density on the nitrogen increases thus increasing the force by which it attracts the hydrogen ion attached to it. The hydroxyl groups of water thus become more movable and the alkaline properties of the solution are strengthened.

We shall consider the properties of amines in more detail using an aromatic amine, aniline, as an example.

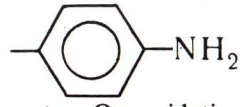
Aniline  . It is a colourless oily liquid sparingly soluble in water. On oxidation it turns light brown and it is poisonous!

Figure IV shows a model of an aniline molecule.

The basic properties are less pronounced in aniline than in ammonia or the amines of the saturated series. Aniline does not change the colour of litmus, however, it yields salts with acids. If concentrated hydrochloric acid is added to

aniline, an exothermic reaction occurs and crystals of a salt precipitate on cooling:

$$C_6H_5NH_2 + HCl \rightarrow [C_6H_5NH_3]Cl$$

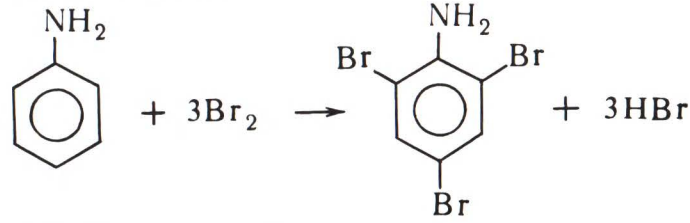
Phenylammonium chloride

If an alkali solution is added to the phenylammonium chloride, aniline is recovered:

$$[C_6H_5NH_3]^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + C_6H_5NH_2 + Na^+ + Cl^-$$

Why is aniline a weaker base than the amines of the saturated series? This is because of the effect of the aromatic radical of phenyl $—C_6H_5$. Remember that the aromatic radical of phenol $C_6H_5OH$ attracts the electrons of the hydroxyl oxygen to strengthen the acid properties of a substance. In this case, the benzene ring attracts the unshared electron pair of the nitrogen from the amino group. The electron density on the nitrogen thus decreases and it attracts the hydrogen ions more weakly. This in turn means that the basic properties of aromatic amines become less pronounced.

We may suggest that the amino group too has an effect on the benzene ring. Bromine (in an aqueous solution) does not react with benzene. But if bromine water is added to aniline solution, a white precipitate of aniline tribromide (aminobenzene tribromide) precipitates:




Earlier we established which group of atoms intensifies the reactivity of the benzene ring; try to remember it.

The action of an oxidizer (e.g. chromic acid mixture) on aniline yields a sequence of substances with different colours. The final product is aniline black, a widespread fast pigment.

Aniline is a very important product of chemical industry. It is a raw material for the manufacture of many aniline dyes and for the preparation of drugs (e.g. sulphanilamides), explosives, and high-molecular compounds.

Zinin, a professor at the University of Kazan, discovered in 1842 a simple method for producing aniline. This method has had a great impact on the chemical industry.

The industry of organic synthesis has begun with the manufacture of dyes. The development of the dye industry became possible on the basis of the reaction for obtaining aniline (the reaction is now known as Zinin's reaction). Aniline is produced simply by reducing nitrobenzene and this can be shown schematically as follows:

$$C_6H_5—NO_2 + 6H \rightarrow C_6H_5—NH_2 + 2H_2O$$

Nikolai Nikolayevich ZININ
(1812–1880)

Zinin was a professor at Kazan University and then at the Surgical Academy in St. Petersburg. He discovered the reaction of the reduction of nitrobenzene to aniline. He synthesized many new organic substances, the products of the reduction of nitrogen compounds.

Zinin founded the Kazan school of organic chemistry. His disciple and successor at the chair of chemistry at Kazan University was Butlerov.

Today aniline is mostly produced by reducing nitrobenzene by metals, e.g. iron (iron chips) in an acid medium.

The general method for preparing amines is the reduction of the corresponding nitrogen compounds.

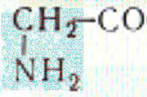
? △

1. Write down the formulas for all the isomers of propylamine $CH_3—CH_2—CH_2—NH_2$.
2. Write down an equation for the combustion of ethylamine, assuming that nitrogen is liberated in the free state in this reaction.
3. The basic properties of dimethylamine are more pronounced than in methylamine. Explain why.
4. Give equations to show the similarity of reactions (a) by which ammonia and amines give salts; (b) by which ammonia and amines are isolated from salts by the action of alkalis.
5. Aromatic amines are weaker bases than amines of the saturated series. Explain.
6. Is diphenylamine $(C_6H_5)_2NH$ a stronger or a weaker base than phenylamine (aniline)? Explain your answer.
7. Arrange diethylamine, aniline, ammonia, ethylamine and diphenylamine in the order of their increasing basicity.
8. How many grams of aniline can be prepared from 246 g of nitrobenzene? (Assume the yield to be 80 per cent).
9. How can aniline be prepared from calcium carbide? Give the scheme of consecutive conversions and specify the conditions for the reactions.
10. Write down the equations for the reduction of (a) nitroethane, (b) nitrotoluene $CH_3C_6H_4NO_2$ to the corresponding amines.
11. Indicate the chemical methods for separating the following mixtures (a) ethyl alcohol and acetic acid; (b) butyl alcohol and phenol; (c) benzene and aniline.
12. Aminophenol is used in photography and has the structure $HO—C_6H_4—NH_2$. Characterize its chemical properties. Give the reaction equations.

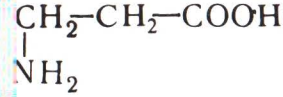
## 10.2 Amino Acids

Some nitrogen compounds have two functional groups. The most important of these are the amino acids.

Structure and Physical Properties. Amino acids are substances whose molecules contain a carboxyl group —COOH and the amino group $-NH_2$. Two examples:



Aminoacetic acid



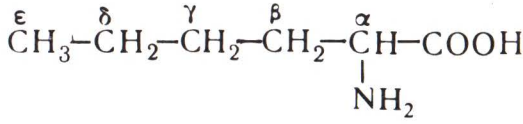
Aminopropionic acid

Figure IV shows models of molecules of amino acids. Amino acids are colourless crystalline substances soluble in water; many of them are sweet.

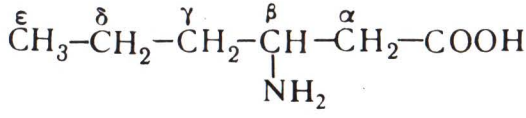
Amino acids can be regarded as carboxylic acids in which the amino group is substituted for the hydrogen atom of the radical. The amino group may be attached to various carbon atoms. This accounts for the isomerism of amino acids. Table 10.1 lists a few amino acids in which the amino group is at the end of the carbon chain.

The greater the number of carbon atoms in the molecule of an amino acid, the greater number of isomers is possible with various positions of the amino group with respect to the carboxyl group.

In order to show the position of the $-NH_2$ group with respect to the carboxyl, the carbon atoms are numbered by the letters of the Greek alphabet:



α-aminocaproic acid



β-aminocaproic acid

Amino acid isomerism is also due to branching of the carbon chain. Draw the structural formulas of some of the amino acids isomeric to aminocaproic acid, that would differ in the structure of their carbon chains.

Amino acids occur widely in nature. While glucose is the basic unit for the high-molecular natural carbohydrates, starch and cellulose, amino acids are the building blocks of plant and animal proteins. The difference is that starch and cellulose are polymerized from one monomer, glucose, while each particular protein is constructed from a variety of amino acids. Amino acids

*Table 10.1*

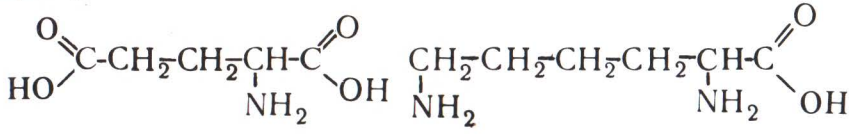
EXAMPLES OF AMINO ACIDS

| Acid | Formula |
|---|---|
| Aminoacetic acid | $H_2N—CH_2—COOH$ |
| Aminopropionic acid | $H_2N—CH_2—CH_2—COOH$ |
| Aminobutyric acid | $H_2N—CH_2—CH_2—CH_2—COOH$ |
| Aminovaleric acid | $H_2N—(CH_2)_4—COOH$ |
| Aminocaproic acid | $H_2N—(CH_2)_5—COOH$ |
| Aminoenanthic acid | $H_2N—(CH_2)_6—COOH$ |

also occur in nature in the free state and as parts of other compounds.

Chemical Properties. What can we conclude about the chemical properties of amino acids from what we know about their structure? Since their molecules contain functional groups whose chemical behaviour we know, we might suppose that amino acids have the properties of both acids and bases. What is the reaction of amino acids to litmus and other indicators? Experiments show that solutions of amino acids are neutral. The action of one functional group on the indicator is probably compensated by the action of the other functional group.

Molecules of some amino acids contain unequal numbers of amino and carboxyl groups, e.g.:



Glutamic acid Lysine

These amino acids act on indicators either as acids or bases, depending on which functional group is prevalent.

Our suggestion that amino acids might be bifunctional is confirmed by their interaction with other substances. Amino acids react like acids with bases to give salts, and react with alcohols to give esters, e.g.:

$$H_2N-CH_2-COOH+NaOH \longrightarrow H_2N-CH_2-COONa+H_2O$$

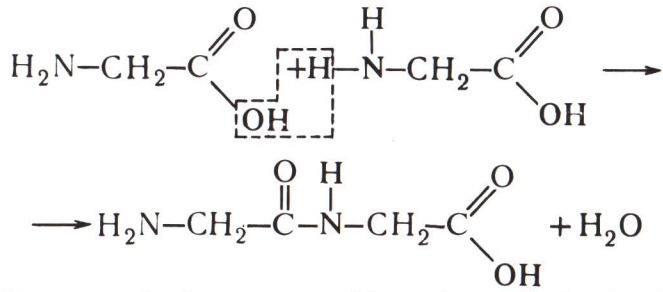
$$H_2N-CH_2-COOH+HOR \longrightarrow H_2N-CH_2-C(=O)-O-R + H_2O$$

Like bases, they react with acids to give salts:

$$H_2N—CH_2—COOH + HCl \rightarrow [H_3N—CH_2—COOH]^+Cl^-$$

Here we meet the amphoteric phenomenon in organic chemistry. *Amino acids are organic amphoteric compounds.*

Amino acids, however, differ substantially from inorganic amphoteric compounds. Since the acid and basic properties of amino acids depend on different groups of atoms, they can react with one another, e.g.:



This molecule can react in the same way with another molecule of amino acid, etc.

The products of this reaction, which is the condensation polymerization reaction (why?), are molecules with many amino-acid monomers. The atom grouping $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$ that is formed during the interaction of amino acid molecules, is called the *peptide* or *amide* group, while the bond between the carbon and nitrogen atoms in it is called a *peptide linkage.*

We shall learn later that amino acid residues are connected into protein molecules by the peptide linkages.

Uses of Amino Acids. Amino acids are needed for the construction of proteins and are obtained by man and animals from their food. However, amino acids can be given as pure substances. They are prescribed to weak and postoperative patients and may be injected straight into the blood. Amino acids are also useful medicines when treating certain diseases. Glutamic acid, for example, is given to patients with nervous diseases, while histidine is given in cases of gastric ulcers.

Some amino acids are used in agriculture to fortify animal feed. They act as growth stimulants.

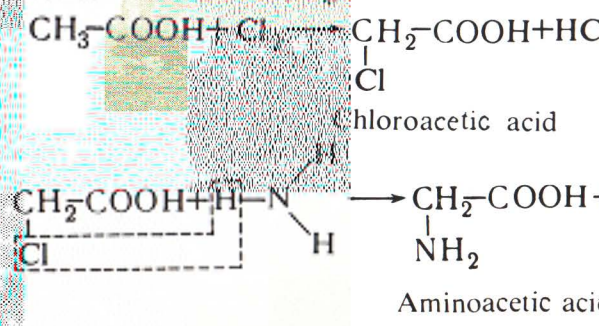
Unbranched amino acids whose functional groups lie at the ends of the molecule are important industrially. The examples are aminocaproic and aminoenanthic acids (see Table 10.1). They are used for making synthetic fibre.

Preparing Amino Acids. Biologically important amino acids can be obtained by hydrolysis of proteins (like glucose is obtained by hydrolysis of high-molecular carbohydrates).

Some amino acids can be prepared synthetically. We shall consider a method by which the relationships between the amino acids and the other known classes of compounds can be established.

A carboxylic acid is a convenient starting substance, and then an amino group can be substituted for a hydrogen atom in its radical. In practice it is best to start by substituting the chlorine atom for one hydrogen atom by chlorination, and then the chlorine atom can be replaced by an amino group by

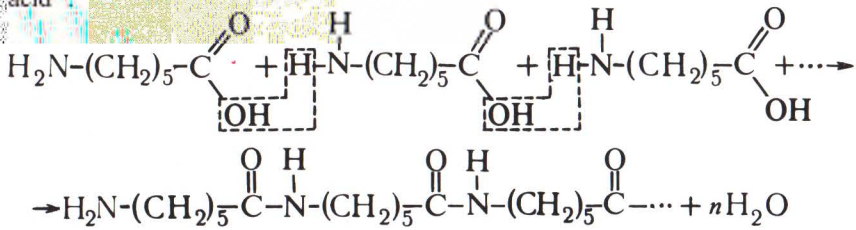
reacting the substance with ammonia, e.g.:



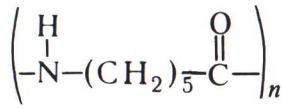
Chloroacetic acid

In the presence of ammonia, chloroacetic acid reacts as an ammonium salt, while the hydrochloric acid forms ammonium chloride.

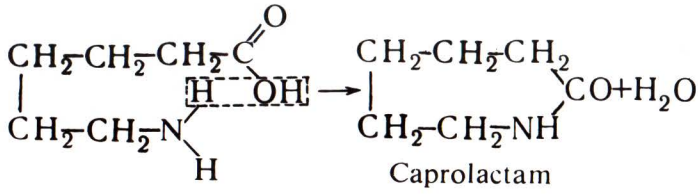
Nylon 6. The polymer from which Nylon 6 is manufactured can be regarded as a product of the condensation polymerization of epsilon-aminocaproic acid*:



Macromolecules of this polymer are linear and consist of repeatedly recurring residues of aminocaproic acid. The structure of this polymer can be expressed as



* In industry, nylon is produced from a derivative of aminocaproic acid, i.e. caprolactam. Caprolactam is the product of interaction of the carboxyl and amino groups inside the amino acid molecule:

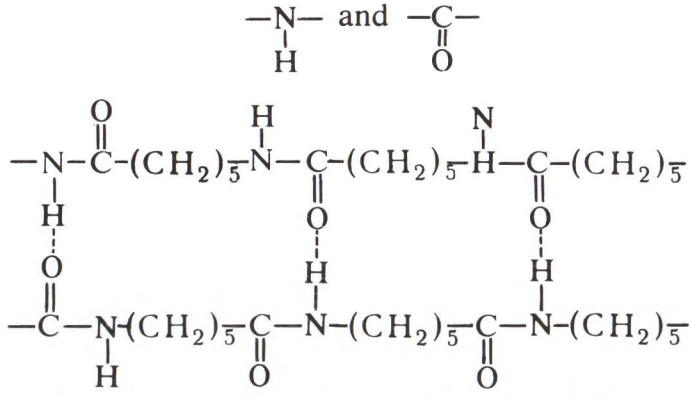


Caprolactam

When the polymer is synthesized, the cycles open at the peptide linkage and combine into linear macromolecules.

The polymer is a resin with its macromolecules arranged at random. In order to rearrange the macromolecules, the resin is melted and passed through dies with fine holes. The jets of the polymer are directed into a shaft in which cold air is delivered from the bottom. The formed fine fibres are then stretched by discs (rotating at different speeds) and spun into threads.

As the fibres are stretched, the molecules orient more and more along the axis of the fibre, and the fibre becomes stronger. The high strength of nylon is also due to the formation of numerous hydrogen bonds that are established between its macromolecules by the interaction of the



Other synthetic fibres are produced from molten polymers in a similar way.

Nylon 6 belongs to the group of polyamide fibres. This name arises because of the amide (peptide) linkages joining the amino acid repeat units together.

The properties of nylon are well known. Nylon articles do not absorb moisture and their strength is not therefore impaired when they are wet. They do not decay, nor are they eaten by moths.

Nylon fibres are wear resistant and can be multiply deformed (flexed) better than natural fibres.

But nylon has some disadvantages. It does not withstand the action of acids (acids hydrolyze their macromolecules at the amide linkages). The heat resistance of nylon is not high either: the nylon fibres lose their strength when heated, and at 215 °C the polymer melts. For this reason nylon garments may not be pressed by a hot iron.

Many of our garments are made of nylon (or mixtures of natural materials containing nylon). Stretch nylon is especially popular. It is used for making stockings, tights, and socks. Nylon is also used to make artificial furs.

Nylon is also used in the manufacture of tyres. Polyamide resins are widely used for making machine parts, bearings, bushings, etc., which are very strong and have high wear resistance.

---

? 1. Which organic compounds have two chemical functions? Give their structural formulas and briefly describe these compounds.

△ 2. Write down the structural formulas of all the isomers of

(a) aminobutyric, and (b) aminovaleric acids.

3. How can ethyl ether be prepared from aminopropionic acid? Write down the reaction equations.
4. Write down the formulas of the two types of salts of aminocaproic acid.
5. How can aminoacetic acid be prepared from methane? Write down the reaction equations.
6. How can alpha-aminopropionic acid be prepared from propyl alcohol (propanol-1)? Write down the reaction equations.
7. The nylon fabric for tyres is stretched out when the tyre is being manufactured. Explain why?
8. The polyamide fibre enanth differs from nylon by being more opaque. It is prepared from the product of condensation polymerization of aminoenanthic acid $H_2N—(CH_2)_6—COOH$. Write down the equation for the condensation polymerization of aminoenanthic acid and give the structural formula for the high-molecular substance formed.
9. Nylon 66 (another polyamide fibre) is obtained by condensation polymerization of hexamethylenediamine $H_2N—(CH_2)_6—NH_2$ and adipic acid $HOOC—(CH_2)_4—COOH$. Write down the reaction equation.

■ 10. Melt a worn out stocking or some other nylon article in a porcelain cup or a tin. Touch the melt with a stick and pull a long fibre. Compare the strength of this fibre with that of the original article.

## 10.3 Proteins

When we studied hydrocarbons and oxygen-containing organic compounds, we also got acquainted not only with low-molecular but also high-molecular compounds. Special emphasis was always laid on synthetic and natural polymers. We also got acquainted with synthetic nitrogen-containing polymers (nylon). Now we shall acquaint ourselves with natural high-molecular nitrogen-containing compounds, proteins.

Proteins in Nature. Proteins are the building block of the living body. They are contained in the protoplasm and the nuclei of all plant and animal cells, and are actually the main carriers of life. Life would be impossible without the proteins. According to Engels's definition, life is the form of existence of proteins.

The molecular weights of proteins range from dozens of thousands to the millions.

The functions of proteins in a living body are quite varied. Proteins are the building blocks of our muscles and skin. Proteins transport substances in the body, e.g. they deliver oxygen from the lungs to the other tissues, and they remove carbon dioxide from the body.

Enzymes (which are also proteins) catalyze numerous chemical reactions inside the body. Hormones (some of them are also proteins) coordinate functions of the body organs. The antibodies that organisms produce to fight infections are also proteins.

A living organism contains thousands of various proteins and each protein performs its own function. Any chemical reaction occurring in the body is

catalyzed by its own protein (enzyme).

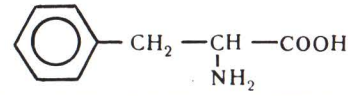
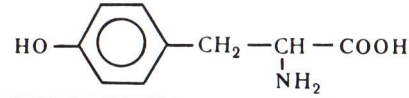
On what does this great variety of the protein functions and their special role in the vital processes depend?

Composition and Structure of Proteins. Most of our information about the composition and structure of proteins has been obtained by studying their hydrolysis. It has been established that hydrolysis of any protein gives a mixture of α-amino acids. Twenty amino acids occur in proteins especially frequently.

The structures of some of the α-amino acids forming proteins are given in Table 10.2.

*Table 10.2*

STRUCTURES OF SOME AMINO ACIDS ISOLATED FROM PROTEINS

| Amino acid | Formula |
|---|---|
| Glycine (Aminoacetic acid) | $H-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$ |
| Alanine | $CH_3-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$ |
| Cysteine | $HS-CH_2-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$ |
| Serine | $HO-CH_2-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$ |
| Glutamic acid | $HOOC-CH_2-CH_2-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$ |
| Lysine | $H_2N-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$ |
| Phenylalanine |  |
| Tyrosine |  |

It is easy to see that the structure of the amino acids that form proteins can be expressed by the general structural formula:

$$R-\underset{\displaystyle NH_2}{\overset{\displaystyle |}{CH}}-COOH$$

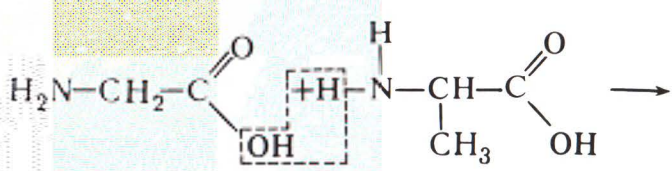
The radical may contain open chains, rings, and other functional groups. The molecules of the amino acids given in the Table contain in their radicals —SH, —OH, —COOH, and $-NH_2$ groups, and even the benzene rings.

How do amino acids form the protein molecule?

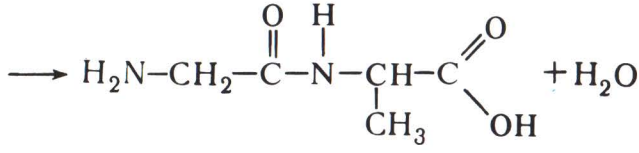
In the 80s of the past century, the Russian biochemist Danilevsky discovered the presence of the peptide groups in a protein molecule. Early in this century, the German investigator Fischer formulated his polypeptide theory, according to which protein molecules are long chains of amino acid residues connected by the peptide (amide) linkages.

Fischer and other investigators synthesized polypeptides whose molecules contained about 20 amino acid residues connected by the peptide linkages. In some of their properties, those polypeptides resembled proteins (e. g. they could be split by enzymes). But they were not proteins.

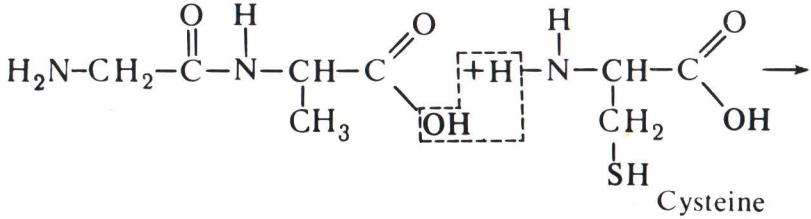
The synthesis of polypeptides can be shown by the following simplified diagram:



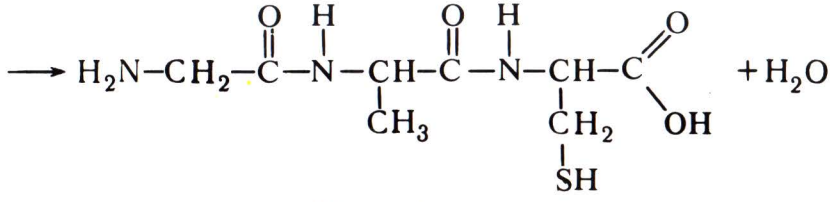
Glycine Alanine



Dipeptide



Cysteine



Tripeptide

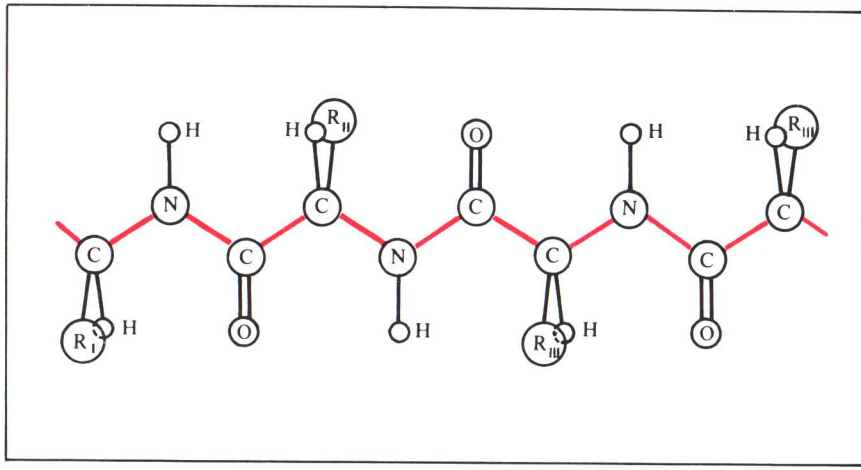



Fig. 54. Primary structure of a protein molecule

The polypeptide theory of protein structure is now accepted universally. Since natural proteins are high-molecular compounds, amino acid residues are repeated many times in their polypeptide chains. Each protein has its own strictly defined sequence of the amino acid residues.

The number of combinations that can be made from the 20 amino acids is practically infinite, just like a multitude of different words constructed from the 26 letters of the English alphabet.

The sequence of amino acids in polypeptide chain is called the *primary structure* of the protein molecule (Fig. 54).

A comparatively small number of proteins have elongated polypeptide chains, like those in the Figure (the protein of natural silk, or fibroin is an example). The chains of overwhelming majority of proteins are coiled into helixes. The spatial configuration of the polypeptide chain is called the *secondary structure* of a protein (Fig. 55). This structure depends on the numerous hydrogen bonds between the —CO— and —NH— groups on the neighbouring coils of the helix.

As the polypeptide chain coils into a helix, the radicals of the amino acid units extend outside. This is very important for the formation of the tertiary structure. The *tertiary structure* is the configuration which the polypeptide chain coiled into a helix assumes in space (Fig. 56).

The tertiary structure is maintained by the interactions between the functional groups of the polypeptide chain radicals. For example, if the carboxyl and amino groups approach each other, a salt bond may be formed, while the carboxyl group and the hydroxyl produce an ester bond, and sulphur atoms form disulphide bonds (—S—S—), etc.

The tertiary structure in the form of a certain spatial configuration of protrusions, depressions, and extended functional groups accounts for the specific biological activity of the protein molecule.

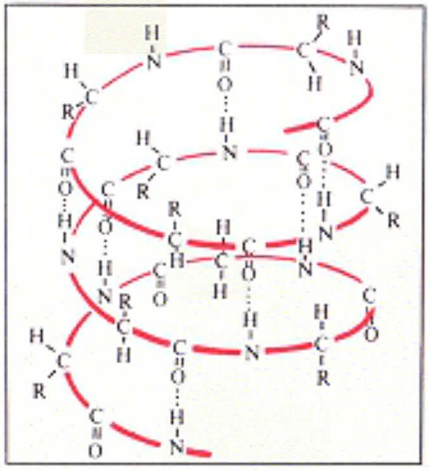


Fig. 55. The secondary (spiral) structure of a protein molecule

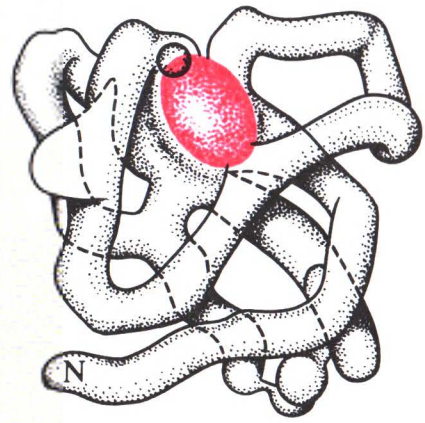


Fig. 56. A model of a molecule of myoglobin protein (tertiary structure)

Because of the presence of the variety of functional groups, proteins cannot be assigned to any particular class of organic compounds; proteins combine the properties of various classes. This combination yields an entirely new quality. Protein is the highest form of development of organic matter.

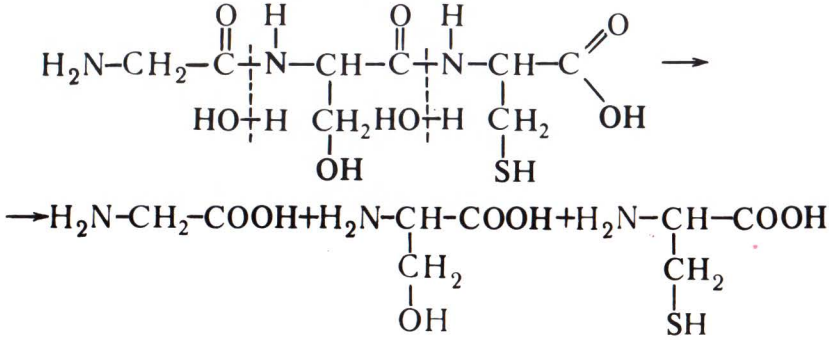
Properties of Proteins. The complicated structure of proteins accounts for their various properties.

Some proteins, for example, egg white, are soluble in water, forming colloidal solutions, others dissolve in dilute salt solutions, while others are completely insoluble.

The presence of the —COOH and $—NH_2$ groups in the protein molecules (in radicals of the amino acid units) makes them amphoteric.

The important property of proteins is their ability to undergo hydrolysis. They can be hydrolyzed either by enzymes or by heating them in the acid or alkaline solutions.

Below is an example of the complete hydrolysis of a tripeptide:



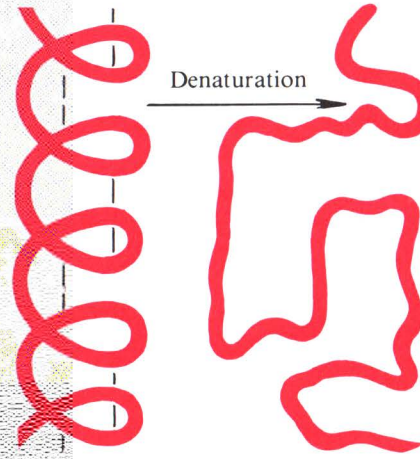



Fig. 57. Denaturation of protein

Using Table 10.2, name the resultant acids.

A similar process occurs when food is digested in the stomach. Under the action of enzymes, proteins are split in the stomach into fragments, again polypeptides, which are further hydrolyzed in the intestine into amino acids. Amino acids are absorbed by the intestinal villi and then delivered by the blood to the tissues and cells of the body. The most of the amino acids are consumed for the synthesis of proteins of the body, the rest are slowly degraded and oxidized.

The action of some factors, such as heat, strong radiation, or even energetic shaking, can distort the configuration of the protein molecule (its secondary and tertiary structures). This is called the *denaturation* of a protein. It consists in destruction of the hydrogen, salt, or other bonds that hold the secondary and tertiary structures. As a result, the protein molecule loses its specific spatial configuration (disorientation) and thus loses its biological properties (Fig. 57). Denaturation of proteins occurs when we boil an egg, or cook food, and in many other processes.

Strong heating not only denatures proteins but can also decompose them with liberation of volatile products that smell of burnt feathers. This smell can be used to identify the proteins.

Proteins give some characteristic colour reactions by which they can be identified. For example, if a concentrated solution of nitric acid is added to a protein solution, the solution turns yellow (due to the nitration of the benzene rings). This reaction occurs on the skin of the hands if the rules for handling acids are neglected and the nitric acid gets on the skin.

Some proteins, which are not food, are used in industry. These are, for example, the proteins of silk, wool, and leather. Describe their practical uses.

Synthesis of Proteins. Investigators have for a long time been searching for ways to synthesize proteins chemically but the first real successes happened only recently.

Why can we not synthesize proteins like we synthesize other high-molecular

substances? The answer lies in the exceedingly complex structure of the protein molecules. In order to prepare a particular protein, it is necessary first to determine its amino acid composition, to establish the primary structure, i.e. the sequence of amino acids in the molecule, to determine the spatial configuration of the protein molecule, and only then to try to reproduce it artificially.

The amino acid composition of proteins is easily established by their hydrolysis. The first protein with deciphered primary structure was insulin (1954). This substance regulates the sugar content of the blood. About ten years were spent to establish the sequence of amino acids in insulin. It was shown that its molecule consists of two polypeptide chains, one of which contains 21 amino acid residues, while the other contains 30 residues. The two chains are connected by two disulphide bonds.

The primary structures of many proteins have now been deciphered. From your course in general biology you should know that the primary structure of ribonuclease protein consists of 124 amino acid residues.

Vasopressin and oxytocin (the hypophysis hormones) were the first artificially synthesized proteins. These are polypeptides with small molecular weight, consisting of nine amino acids each.

The chemical synthesis of insulin and ribonuclease is an important event in chemistry. The extraordinary complexity of this synthesis can be illustrated by the fact that 89 reactions are required to synthesize one of insulin's polypeptide chains, while 138 reactions are required to synthesize the other.

The biosynthesis of proteins by microorganisms is now being used on an ever increasing scale. When cultivated on a suitable nutrient medium, some microorganisms can produce vast quantities of proteins. The wastes of alcohol manufacture (from cellulose) can be used to cultivate fodder yeast. Petroleum paraffins are also used for the microbiological synthesis of proteins. Microorganisms can produce some other valuable substances, such as amino acids and vitamins. Using products of microbiological synthesis increases the efficiency of animal husbandry.

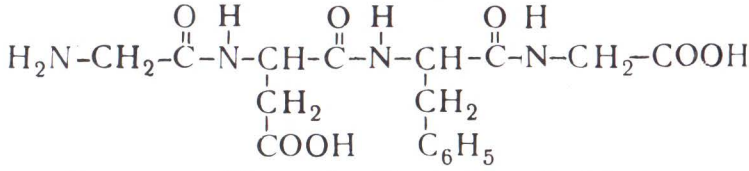
While searching for ways to synthesize proteins, investigators study how it is synthesized by living organisms. The process occurs here in "mild" conditions and at a surprisingly high rate (a molecule of protein is produced by a cell in 2–3 seconds).

In future, when man discovers the mystery of natural biosynthesis of proteins, artificial manufacture of proteins will probably be based on the same principles that underlie the processes occurring in the living cell.

The discovery of the mechanisms of the finest processes occurring at the molecular level in the living body, is one of the most important and fascinating aspects of science nowadays. Advances in this field will raise man still higher above nature, and immense resources for preparing various valuable materials will be discovered in future. Man will master those processes which now occur only in a living cell. Inexhaustible sources of energy released by chemical reactions will be discovered. Man's diseases will be eradicated and man will live a longer life.

? 1. Determine approximately the molecular weight of a protein containing 0.32 per cent of sulphur, assuming that its molecule contains only one sulphur atom.

△ 2. Write down the formulas and name the substances that are formed by the hydrolysis of the following compound:



3. How many different tripeptides can be obtained by various combinations of three amino acid residues? Take three amino acids from Table 10.2 and write down the formulas for all the tripeptides that can be formed.
4. Assume that all the amino acids indicated in Table 10.2 are contained in a molecule of a protein. Give all the reactions that in your opinion might be characteristic of this protein.
5. What role does hydrogen bonding play in the structure of a protein molecule? What other examples can you give to illustrate the dependence of the properties of substances on the presence of hydrogen bonds in them?
6. What is meant by the denaturation of proteins? What causes denaturation? Has denaturation any practical importance?
7. What substances are produced during the hydrolysis of (a) fats, (b) carbohydrates, (c) proteins in a living body?
8. Why cannot protein foods be replaced for a long time by food containing only fats and carbohydrates?

■ 9. Milk contains all three main groups of nutrients, namely proteins, fats, and carbohydrates. Separate the fat from milk. Next add an acid to the remaining milk to isolate the protein. Compare the behaviour of sour milk during heating it in the presence and absence of baking soda. Explain your observations.
10. What is the simplest method to differentiate (a) a woolen thread from a cotton thread; (b) natural silk from viscose rayon; (c) natural leather from its substitutes.

## Conclusion

During our study of organic chemistry we have covered a great deal of new material about substances, we have studied the major classes of organic compounds, the causes of their great variety, and we have considered the structure and properties of organic substances and their increasing importance in our lives. It is time now to come to some conclusions and make some generalizations. Let us revise what we know in organic chemistry and how this knowledge has influenced our theoretical concepts.

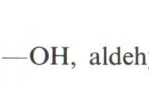
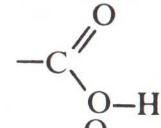
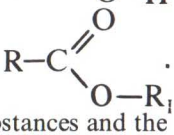
The Structure and Properties of Organic Substances. The foundation for the theory of the structure of organic substances was laid by Butlerov. He developed the theory of chemical structure, that substantiated the sequence in which atoms are combined in molecules. It was later enriched with the

stereochemical theory which explained the spatial arrangement of atoms in molecules, and still later by the electron theory which demonstrated the character of the interatomic connections in molecules. These three theories are closely related and form the essence of the modern theory of structure.

The theory of chemical structure discusses the sequence of the atoms in molecules and how the properties of substances depend on this sequence. The sequence of atoms is implied to be the order of their mutual effects on one another. These mutual effects were explained later by the electron theory.

What types of atom sequence determine their molecular properties? The structure of organic substances depends on the ability of carbon atoms to unite together in chains. These chains may be open or closed in rings (cycles); open chains may be linear or branched; cyclic structures may combine with open chains, etc. When discussing the character of carbon chains we saw how the properties of a substance depend on the sequence of atoms in the molecules. Substances may have the same molecular composition, but their carbon chains may differ, and this is why they will have different properties. Try to remember the differences in the properties of isomers of the saturated hydrocarbons.

We know that the bonds between atoms are also different. They may be single (ordinary) bonds, or multiple (double or triple) bonds. The sequence of bonds in a molecule may be different as well. This is also important for the properties of substances. It can easily be shown that this is so by comparing the properties of saturated and unsaturated hydrocarbons, or the properties of unsaturated hydrocarbons with double bonds in different positions.

If organic substances contain chemical elements other than carbon and hydrogen, new atom sequences are formed. We know several *functional groups*, such as hydroxyl —OH, aldehyde  , carboxyl  , amino $—NH_2$, atom groupings of ethers $R—O—R_1$ and esters  .

All these groups of atoms determine the properties of the substances and the class of chemical compounds to which they belong.

Now we can fully appreciate the importance of the sequence of atoms in molecules and its effect on the properties of substances.

*Homology* and *isomerism* are very important concepts in the theory of chemical structure. In addition to the ability of carbon atoms to form chains, these concepts explain why there is such a great variety of organic compounds. Define homology and isomerism. Give examples of homologous series of hydrocarbons and oxygen-containing organic substances.

Several types of isomerism are known to us. Let us name them.

(a) Nuclear or chain isomerism. We have discussed this type of isomerism in detail during the study of the saturated hydrocarbons and we pointed out the effect of the order in which carbon atoms are arranged in the molecule on the physical properties of the substances. Write down the structural formulas of the

hexane isomers. This type of isomerism is also seen in substances belonging to other classes of organic compounds. Which isomers with the formula $C_5H_{11}OH$ do you know?

(b) Position isomerism. The difference in the structure of some substances depends on the position of the multiple bond. We considered this type of isomerism when we studied unsaturated hydrocarbons. Give the structural formulas of hexene-1, hexene-2, and hexene-3. Illustrate this type of isomerism with the formulas of unsaturated carboxylic acids.

(c) Isomerism due to the position of a substitute in the carbon chain. Remember the structures of 1-bromopropane and 2-bromopropane, and butanol-1 and butanol-2.

(d) Functional group isomerism. We observed this type of isomerism in some oxygen-containing organic compounds, e. g. in carboxylic acids with substitutes (halogens) at various positions in the hydrocarbon radical. We met this sort of isomerism during our study of amino acids. Give the structural formulas of the isomers of aminocaproic acids.

(e) Isomerism of substances belonging to different classes of organic compounds. Remember that the ethylene hydrocarbons are isomeric to the cycloparaffins (with equal number of carbon atoms in the molecule), the acetylene hydrocarbons are isomeric to diene hydrocarbons, the monohydric alcohols to the ethers, and monocarboxylic acids to the esters. Illustrate these isomers by structural formulas.

*Stereochemical theory* discloses the spatial arrangement of atoms in molecules and explains many phenomena that were not understood earlier. It appeared that the four valency bonds of the carbon atom are directed toward the vertices of the tetrahedron and this accounts for the tetrahedral structure of the methane molecule and the zigzag structure of the carbon chain. Since atoms can rotate about single bonds, the carbon chain can assume various spatial configurations.

Another type of isomerism has been discussed. This is *geometrical* or *cis-trans* isomerism and it occurs in compounds with a double bond between two carbon atoms each of which is connected to dissimilar atoms or groups of atoms. Give the structure of 1,2-dichloroethane and butene-2 to illustrate the *cis-trans* isomerism. Geometrical isomerism explains the structure of natural rubber, the cause of its high elasticity, and why many investigators failed to obtain synthetic rubber that could rival natural rubber. When we studied the spatial structure of macromolecules, we understood the causes of different properties of rubber and cellulose, although both substances have linear structures. We showed the complexity of spatial structure of protein molecules upon which their variety of functions depend.

The *electron theory* is a tool by which we can understand more deeply the structure of substances and the essence of chemical conversions. Many problems that were difficult to solve using the previous theories became explainable from a consideration of the electron structure of atoms and the electron nature of chemical bonds. Why does the order in which the atoms are arranged in the molecule affect the properties of substances? What is the essence of mutual effects of atoms on each other? Why are valency bonds of the carbon atom directed to the vertices of the tetrahedron? Why are multiple

bonds more reactive than single bonds? Benzene is a very unsaturated compound in composition. Why does benzene have the properties characteristic of both saturated and unsaturated hydrocarbons then?

The electron theory makes it possible to discuss in more detail the effect the electron structure of the molecule has on the properties of the substance. The effects atoms have on each other explain the appearance of new properties, which are not simply the summation of the properties of the elements that compose the molecule. The essence of this effect is the interaction of electron structures of the atoms.

When we discussed simple halogen substituted hydrocarbons, we saw that the inclusion of the halogen atom in the molecule alters its properties. The chlorine atom in methyl chloride attracts the electron density of the C—Cl bond. This shifts the electron density of the C—H bond in the direction of the carbon atom. As a result, further substitutions of the hydrogen atoms in the molecule become easier. The properties of the chlorine atom are also affected once it has become bonded to the carbon atom: it becomes unable to participate in ion-exchange reactions (as in HCl or NaCl).

Our study of the electron effects inside molecules helped us understand the Markownikoff rule. Once you know that the hydrocarbon radical can repel the electron density in the $\sigma$ bond, explain why the addition of HCl to the propylene occurs according to the following scheme

$$CH_3—CH=CH_2 + HCl \rightarrow CH_3—CHCl—CH_3$$

Again the atoms affect each other: the halogens can comparatively easily (at elevated temperatures) substitute the hydrogen atoms in the hydrocarbon radical of propylene. Consider (consulting the textbook if necessary) the mutual effect of atoms in organic molecules you know. Compare, for example, the properties of benzene, phenol, and ethyl alcohol; monohydric alcohol, phenol, and a carboxylic acid; saturated amines, ammonia, and aromatic amines. Answer the following questions. Why do alcohols have acid properties? Why do they dissociate less than water? Why does the dissociation degree increase if a halogen atom is added to the hydrocarbon radical? Why has phenol stronger acid properties than alcohols, while the acid properties of carboxylic acids are even stronger? Why is the formic acid the strongest monocarboxylic acid? How does the position of a halogen atom at the acid radical affect the acid's degree of dissociation? Why are saturated amines stronger and aromatic amines weaker bases than ammonia?

We can now conclude that the properties of organic substances depend on their composition, and their chemical, spatial, and electronic structure.

Now let us generalize our knowledge of the major properties of organic substances. Using this textbook describe the following chemical reactions (write them down in your copy-book):

(a) reactions of saturated hydrocarbons: combustion; decomposition into the simple substances; substitution; dehydrogenation; dehydrocyclization; isomerization; and oxidation to carboxylic acids;

(b) reactions of unsaturated hydrocarbons: hydrogenation; halogenation; addition of hydrogen halides and water; and polymerization;

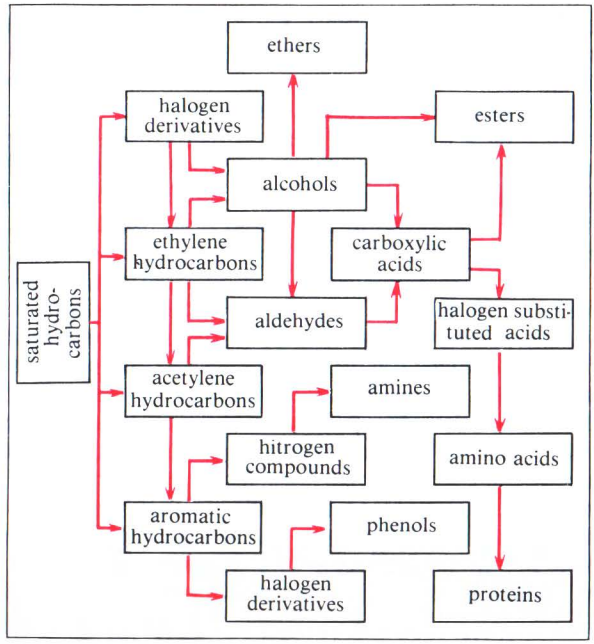



Fig. 58. Genetic ties between organic compounds

(c) reactions of aromatic hydrocarbons: addition and substitution (benzene); oxidation and substitution (toluene);

(d) reactions of monohydric alcohols: with the alkali metals; with hydrogen halides; reactions of inter- and intramolecular dehydration, oxidation, and esterification;

(e) reactions of aldehydes: oxidation and reduction;

(f) reactions of carboxylic acids: with metals; with metal oxides; with bases; and esterification reactions;

(g) reactions of esters: hydrolysis.

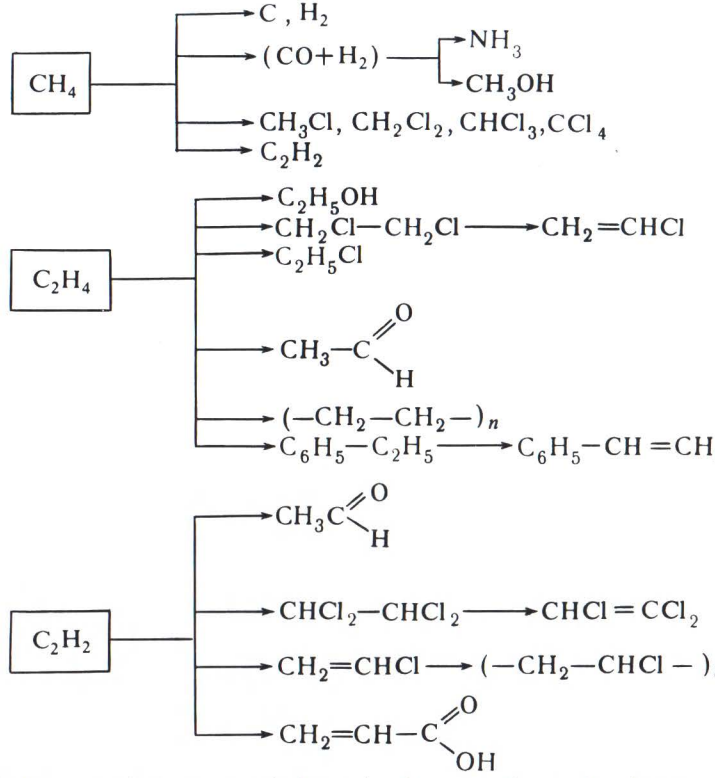
Name reactions for substances of the other classes that you know. As we discussed the chemical properties of substances, we could notice that organic substances of different classes can be converted into each other through consecutive conversions. Almost all substances can be obtained in some way from simpler hydrocarbons. This chain of consecutive conversions originating from hydrocarbons and extending to most complex organic compounds can be followed in the scheme in Fig. 58. The hydrocarbons that are the basis of organic compounds can be synthesized from carbon and hydrogen. This means that organic substances are related to inorganic substances.

Organic Synthesis Industry. The hydrocarbons can be converted into every other sort of organic substances not only in the laboratory (theoretically). Many of the organic substances, which are very important for national economy, are now produced industrially from hydrocarbons.

Petroleum and natural gas are the two major sources of these hydrocarbons

*Table 11*

THE INDUSTRIAL SYNTHESIS OF COMPOUNDS FROM HYDROCARBON GASES




and the chemical conversions are carried out in the *petrochemical industry*. Large quantities of synthetic materials are turned out by this industry: halogen substituted hydrocarbons, alcohols, phenols, aldehydes, ketones, carboxylic acids and their derivatives, monomers for the synthesis of polymers, synthetic detergents, chemical poisons, etc.

But the sources of petroleum are limited, and efforts are now being taken to decrease the amount of petroleum spent to generate energy in order to increase the share of petroleum used to obtain more valuable materials. The importance of the hydrocarbon raw materials for the modern industry can be seen from Table 11 (the processes known to the student from this course of organic chemistry are mainly given in the table). The organic synthesis industry increases its output from year to year, but it also improves the quality of its goods.

The requirements of modern technology for various substances and materials become more exacting. The organic synthesis industry in cooperation with inorganic chemistry do their best to solve this problem. For example, heat-resistant plastics, materials that can stand corrosive media, synthetic fibres

with a variety of properties, and frost- and wear-resistant rubbers that are impermeable to gas are all produced today.

More efficient chemical processes, that are realized in fewer steps, are replacing multi-stage processes. We have seen, for example, how acetylene is being produced from methane, carboxylic acids by the direct oxidation of hydrocarbons, and acetaldehyde by the oxidation of ethylene (compare this process with the manufacture of acetaldehyde from calcium carbide).

Batch processes are replaced by continuous processes to ensure higher efficiency of labour. Cracking of petroleum products is now realized at continuous plants. Polymers are produced in continuous reactors as well. You should already know about other continuous processes.

Almost all the processes for preparing the organic substances are catalyzed. Efficient catalysts, especially selective ones, are therefore always being sought. You should now know that reactions between organic substances often give many various products. Catalysts are therefore required which can accelerate only those reactions by which the required products are produced.

Reduction of wastes is an important problem. This saves a great deal of materials, ensures their complete utilization, and saves the environment from industrial pollution. If certain side products cannot be utilized, they can be destroyed in effluents by adding some reagents, or by microbiological methods. Many chemical plants have closed water supply systems: their liquid wastes are not discharged but are purified and reused. The environment is thus protected from accidental pollution. New plants are so designed that they produce no wastes. This is also done to improve the protection of the environment.

Continuous chemical processes should be automated as much as possible. The chemical industry is now one of the most automated. This is very important for the labour hygiene. Every chemical process occurs in sealed plants. All parameters that are important for the chemical processes (flow rates, temperature, pressure, etc.) are controlled automatically. Control panels are installed in special rooms, where the operator reads the instruments, and takes all the necessary measures to preclude deviations from process specifications. In order to manage a chemical process, the operator should be well educated in chemistry, chemical technology, and other sciences.

The Place of Organic Chemistry Among Natural Sciences. Together with other sciences, chemistry helps in the formation of our dialectical and materialistic concepts. By treating the chemical form of motion of matter, chemistry gives us knowledge of the world of substances. This is necessary for understanding the life of nature. Organic chemistry is intermediate *between inorganic chemistry and biology*. It explains the gradual complication of substances, their varied conversions, it helps understand the evolution of matter in nature and the material basis of life and the essence of the higher form of motion of matter, the biological form.

We can see that like inorganic substances, all organic substances are related. Each organic compound belongs to a definite class, but all the classes are related to each other. Organic compounds are related to inorganic compounds: they can be synthesized from them and be decomposed into inorganic substances.

A study of the theory of structure shows that science penetrates the inner world of atoms and molecules to reveal deeper phenomena and regularities of the microworld. None doubts today the existence of atoms and molecules. Moreover, we know about the sequence of atoms in molecules, their arrangement in space, the character of the interatomic bonds, the influence that the atoms have upon each other, the electron mechanism of chemical conversions, etc. Our knowledge and its objective character are verified by experiments. Many substances are synthesized by man on the basis of the theory. We know that all chemical conversions are based on material processes occurring in the microworld that are governed by objective laws of the structure of matter rather than by some immaterial forces. All this strengthens our position in the materialistic understanding of the world.

It also shows that the inner world of matter is understandable and that our knowledge develops from observation of a phenomenon to deeper understanding of its essense (remember the stages in the development of the theory of structure).

As we studied the theories of chemical structure, spatial and electron structure of substances, we came across a general regularity: the development of theoretical knowledge through the resolution of contradictions between the older theory and new facts, when the old theory becomes unable to explain these new facts. We remember that the theory of chemical structure, and later the theory of electron structure, explained many facts that were unexplainable by the old theory.

The study of organic chemistry has enriched our knowledge of the effect of quantitative changes on quality. We learned that adding one or two $CH_2$ groups to a molecule results in the formation of homologues. The properties of substances change with increasing numbers of similar functional groups. The characteristics of monomers change when they are united into polymers.

We know that new quality, i.e. a new substance, is formed not by the mechanical addition of groups of atoms, but by the interaction of the component parts of molecules, and by the mutual influences of atoms in the molecule, which shows itself in electron shifts. The appearance of a new substance is thus an entirely materialistic phenomenon. The properties of molecules are not the sum of the properties of the parent atoms. A molecule is an entirely new quality. Likewise, the opposite phenomena, such as the reactivity of functional groups and the relative stability of radicals are not independent of each other. We can see that the radical affects the properties of a functional group and its own properties are affected by the functional group (compare, for example, the properties of benzene and phenol, and the properties of the saturated and aromatic amines).

But organic chemistry studies nature not only to broaden our scientific picture of the world. By giving us knowledge about substances and the laws that govern their interconversions, organic chemistry gives us tools to synthesize substances that are not found in nature or occur only in scarce amounts. Together with other sciences, organic chemistry becomes a powerful creative force.

# Laboratory Exercises

## 1. Making the Models of Hydrocarbon Molecules

1. Methane Molecule. Take a piece of light plasticine and shape it into four small balls. Use a darker plasticine to make a ball with a diameter about one and a half times greater. This will approximately correspond to the relative dimensions of the hydrogen and carbon atoms. Pierce four matches into the "carbon" ball at about equidistant points so that the matches extend in the direction of the vertices of a tetrahedron. Now pierce the free ends of the matches into the "hydrogens" and press the balls together so that they flatten slightly: this will imitate the overlapping of the electron clouds that interconnect the atoms in the molecule.

2. Propane Molecule. Remove one "hydrogen" from the methane molecule and attach another "carbon" with two "hydrogens". Now attach the third carbon to the free fourth point of the second carbon, and finally attach the hydrogens to complete the model of propane. The initial stage of formation of a zigzag can thus be seen in this model.

3. Butane and Isobutane Molecules. Construct these models following the instructions given above. Compare them with those shown in Fig. 7. Make sure that the models are robust. See if the atoms can rotate about the C—C bonds.

## 2. Properties of Polyethylene

1. Heat slightly a specimen of polyethylene by holding it in forceps over an alcohol or a gas burner: polyethylene first softens and then melts. Using a glass rod, shape the molten mass into any configuration and allow to cool. Try to change the shape of the polyethylene sample when it is cold.

What property of polyethylene is illustrated by this experiment?

2. Set fire to a specimen of polyethylene. Does it burn within or outside the flame of the burner? What is the colour of the flame? Does polyethylene produce soot? Do the products of polyethylene combustion smell of anything?

3. Place bromine water and potassium permanganate solution into separate test tubes and see what action they have on granules or small pieces of polyethylene. Do the colours of the solutions change? Do these solutions act on the polymer?

4. Place sulphuric acid and sodium hydroxide into separate test tubes and add pieces of polyethylene.

What conclusion on the chemical properties of the polymer can be made from the results of these experiments?

## 3. Properties of Rubber and Cured Rubber

1. Cut out two narrow strips of crude and vulcanized (cured) rubber making sure that both have the same cross section and length. Stretch and then release them. Which specimen shrinks to its initial shape first? Which of them is more elastic?

Stretch the specimens until they break. Which rubber is stronger?

2. Place 2-3 ml of petrol into two test tubes. Drop a piece of rubber into one test tube and a piece of vulcanized rubber into the other. Close them with cork stoppers and allow to stand until the next lesson. What changes occur? How can the different solubilities of the two rubbers in petrol be explained?

## 4. Properties of Glycerol

1. Place 1 ml of water in a test tube, add an equal volume of glycerol and shake the mixture. Now add the same amount of glycerol. Characterize the solubility of glycerol in water.

2. Place 2 or 3 drops of glycerol on a sheet of blotting paper and on another part put a few drops of water. Observe from time to time, which of the fluids evaporates first? Explain the results of the experiment.

3. Place 2 ml of sodium hydroxide into a test tube and add a few drops of copper(II) sulphate solution. Add glycerol to the formed copper(II) hydroxide and shake the mixture. Observe the changes and make the corresponding conclusions.

## 5. Properties of Formaldehyde

1. Wash a test tube thoroughly with a soda solution and rinse with distilled water. Place 1 ml of ammoniacal solution of silver(I) oxide,* and add 4-5 drops of dilute formaldehyde down the wall of the test tube. Place the test tube into a beaker containing hot water: silver metal should deposit on the test tube walls. Write down the reaction equation.

2. Place 3-4 drops of copper(II) sulphate solution into a test tube and add 2-3 ml of sodium hydroxide solution. Add 1-2 ml of dilute formaldehyde to the precipitate formed and heat the mixture. How does the colour of the precipitate change? Write down the equations for reactions between the copper sulphate and the alkali, and between the formed precipitate and formaldehyde.

## 6. Oxidation of Alcohol to Aldehyde

1. Make a spiral of 5 or 6 coils at the end of a piece of copper wire.

2. Place not more than 1 ml of ethyl alcohol into a test tube, heat the copper spiral over a burner until the copper becomes coated with black scale, and immerse the wire into the alcohol quickly. Repeat the procedure several times. Note the smell of the aldehyde formed, and the changes occurring on the spiral.

3. Write down the equations for the oxidation of copper during the heating and the oxidation of the alcohol to aldehyde by copper(II) oxide.

## 7. Properties of Fats

1. Place 1 ml portions of water, alcohol, and petrol into separate test tubes and add about equal portions of solid fat or

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* Prepare the silver oxide solution by adding 25% ammonia solution (diluted ten times with distilled water) to a 2% silver nitrate solution until the precipitate dissolves.

a few drops of vegetable oil into each test tube. Observe the reaction in each test tube after shaking. In which liquid will the fat dissolve better?

2. Transfer a few drops of the fat dissolved in alcohol and that dissolved in petrol onto a sheet of blotting paper. What remains on the paper after the evaporation of the solvent?

## 8. Properties of Soaps and Synthetic Detergents

Prepare 25-30 ml of 1% solutions of common soap and of a synthetic detergent (powder) in distilled water. Place 3-4 ml of hard water in two test tubes. Add the soap solution to one test tube and the detergent solution to the other test tube, drop by drop. Shake the solutions after each drop. In which test tube does the lather begin to form first? Which solution retains its washing properties in hard water?

## 9. Properties of Glucose

1. Place 3-4 drops of copper(II) sulphate into a test tube and add 2-3 ml of sodium hydroxide solution. Add an equal volume of glucose solution to the resultant hydroxide and shake. How does the colour of the solution change? Why?

2. Heat the test tube contents, and observe the changes. The presence of which functional group in the glucose molecule does this experiment confirm? Write down the equation for the oxidation of glucose by copper hydroxide.

3. Place some ammoniacal solution of silver(I) oxide into a clean test tube and add half the volume of glucose solution. Heat the mixture carefully over a burner. Heat slowly and uniformly. Observe the changes, and explain them.

## 10. Reaction of Sucrose with Metal Hydroxides

1. Prepare a small quantity of copper(II) hydroxide as instructed earlier. Add some sucrose (sugar) solution and shake. How does the colour of the solution change? Explain the reaction.

2. Place a 20 per cent sugar solution into a beaker and stir in small portions of milk of lime. Does the lime dissolve? Explain your observations.

## 11. Properties of Starch

1. Place some pure starch into a test tube, add water, and shake well. Pour the suspension slowly into some hot water in a beaker stirring it all the time and boil: a starch size is formed.

2. Place 2-3 ml of the size into a test tube, dilute with water, and add a drop of alcoholic iodine solution. Observe the changes.

3. Heat the mixture and observe the changes again. Is the initial colour restored if the mixture is cooled?

4. Heat starch size in a test tube together with freshly precipitated copper(II) hydroxide. Is copper hydroxide reduced by starch?

5. Chew up a piece of rye bread and place a small portion of this mass into a test tube. Add a few drops of copper sulphate and alkali solution to precipitate the copper hydroxide. Heat the mixture and observe the changes. Explain your observations.

### 12. Properties of Proteins

1. Place 2 ml of a protein solution in a test tube and add an equal volume of sodium hydroxide solution and then a few drops of a dilute blue vitriol solution. The protein turns red-violet.

2. Place a small quantity of ground meat in water into a beaker and boil. Separate the liquid on a cotton wool filter and see if it contains protein by testing it by a colour reaction.

3. Burn some threads and decide if the fabric they came from is cotton or woollen?

# Practical Experiments

### 1. Identification of Carbon, Hydrogen, and Chlorine in Organic Substances

1. The qualitative composition of liquid and solid hydrocarbons can be determined by oxidizing them with copper(II) oxide.

Place 1 g of copper oxide powder in a dry test tube and add a small portion (0.2 g) of paraffin wax, kerosine, or vaseline. The liquid petroleum products should impregnate copper oxide powder. To that end, paraffin wax in the test tube should be heated.

Fix the test tube in the horizontal position, add a small quantity of anhydrous copper sulphate, and close the tube with a stopper through which a gas tube is passed. See to it that the copper sulphate powder is near the stopper. Lower the other end of the gas tube into lime water in a test tube (Fig. 59).

Heat the test tube contents gently over a burner. What can be seen on the walls of the test tube? What changes occur in copper sulphate and lime water? Discontinue heating, and allow the test tube to cool. Remove the copper sulphate and reaction products. Into what has the initial copper oxide been converted during oxidation of hydrocarbons?

What conclusion on the qualitative composition of the petroleum products can be made from the experiment? Write down the equation for the complete oxidation of the saturated hydrocarbon by copper oxide (the hydrocarbon contains 14 carbon atoms).

2. The presence of chlorine can be revealed by heating the organic compound with copper: chlorine forms a volatile salt with copper, which colours the flame a characteristic green.

Make a spiral at the end of a copper wire, heat it over a burner until the flame is no longer coloured.

Touch the test liquid with the spiral (for example, 2-3 drops of dichloroethane or tetrachloromethane) and place into the flame again. The green colour of the flame indicates the presence of chlorine in the organic solvent.

Try another sample for the presence of chlorine.

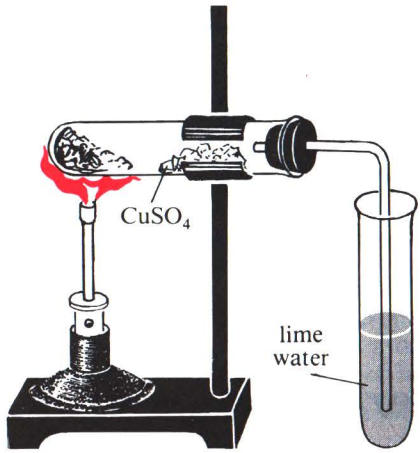


Fig. 59. Identifying carbon and hydrogen in hydrocarbons

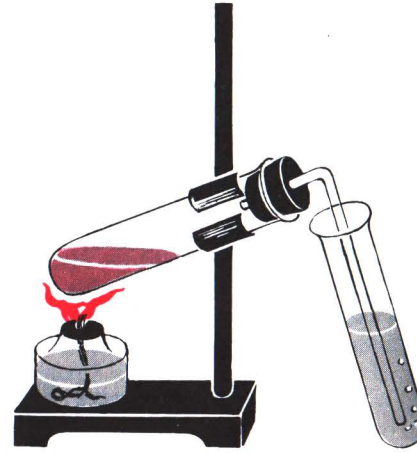

Fig. 60. Preparing ethylene

## 2. Preparing and Experimenting Ethylene

Write down an equation for the reaction by which ethylene is formed (heating ethyl alcohol with sulphuric acid).

Assemble the apparatus shown in Fig. 60 and test it for tightness. Place 5 ml of a mixture of alcohol and sulphuric acid (one volume of alcohol to three volumes of sulphuric acid) in a test tube or a flask, add a small portion of calcined sand or pumice to avoid vigorous boiling, close the test tube with a stopper through which a gas tube is passed, and fasten the apparatus in a tripod as shown in the picture. Heat the mixture carefully!

When the reaction begins, pass the liberated gas into 2-3 ml (not more) of bromine water. See to it that the gas tube end reaches the bottom of the test tube containing the bromine water.

The heating should be continuous, otherwise the bromine water may be sucked into the apparatus. What changes occur in the bromine water?

Pass ethylene into the test tube containing the same amount of acidified potassium permanganate solution. Observe the changes.

Remove the gas outlet tube from the solution, turn it upward, and light the evolving gas. Does it burn with a luminous flame?

Turn off the burner: ethylene liberation discontinues.

Explain the observed phenomena. Write down the equations for the reactions.

## 3. Obtaining Ethyl Bromide

Write down the equations for reactions by which ethyl bromide is prepared from a mixture of ethyl alcohol, sulphuric acid, and potassium bromide.

Assemble the apparatus shown in Fig. 61. If a water tap is available at the laboratory bench, use a water-cooled condenser instead of the air-cooled one,

because ethyl bromide is very volatile (b.p. 38.4 °C) and intense cooling is required to condense it.

Place a mixture of ethyl alcohol and sulphuric acid (8-10 ml) into a 50-100 ml flask, add gradually 3 ml of water and 5 g of potassium bromide (or sodium bromide). Close the flask with a stopper connected to a condenser, and lower the other end of the condenser into a flask or a test tube containing a mixture of ice and water.

Heat the mixture carefully on a water bath or over a burner on a gauze with an asbestos centre. Observe condensation of ethyl bromide vapour in the condenser and formation of a layer of heavy liquid under the water in the receptacle.

When the oily liquid stops dripping into the receptacle, put the condenser aside and stop heating.

The receptacle contents (without the ice) should be transferred to a separating funnel. Allow the liquid to settle and separate the lower layer of ethyl bromide. Give the product of your experiment to the teacher.

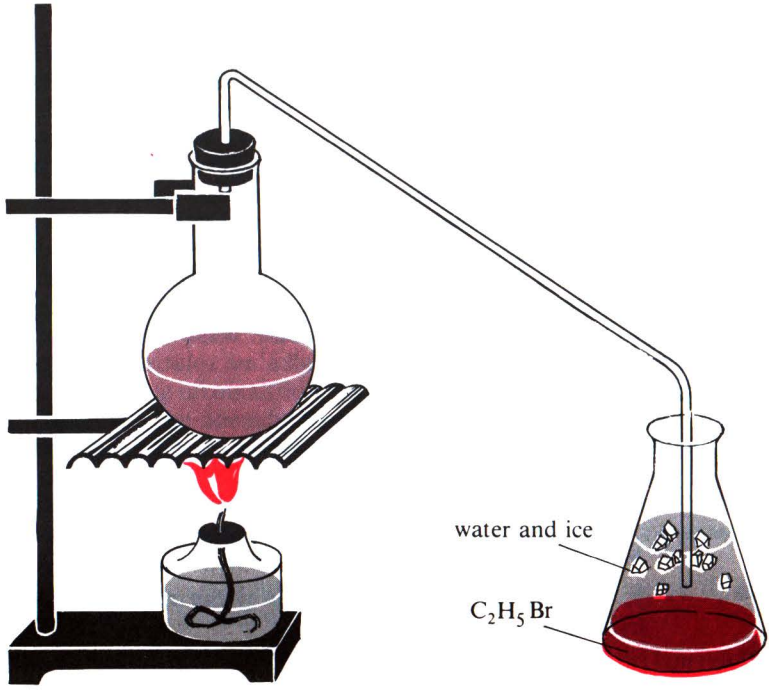


Fig. 61. Preparing ethyl bromide

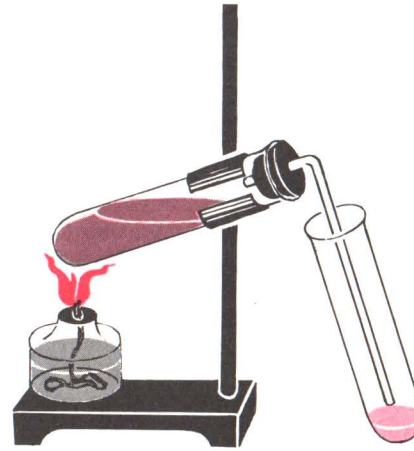

Fig. 62. Preparing acetic acid

## 4. Preparing Carboxylic Acids

1. Place 3-4 g of sodium acetate into a test tube, add about 2-3 ml of sulphuric acid (1 : 1) and close the test tube with a stopper through which a gas tube is passed. Lower the free end of the gas tube into an empty test tube (Fig. 62). Heat the mixture over a burner until 1-2 ml of liquid are collected in the receptacle. Pay attention to the odour of acetic acid.

2. Divide the collected acid into two portions. Try one portion with litmus and neutralize with alkali solution. Dilute the other portion with a small amount of water, and put some magnesium ribbon (or powder) into the solution. Describe your observations and write down the reaction equation.

3. Try the action of acetic acid on any other metal oxide or salt.

4. See if formic acid is oxidized by an ammoniacal solution of silver(I) oxide. Write down the reaction equation.

5. Prepare a solution of a common soap by heating some soap chips in water in a test tube.

6. Place 2-3 ml of the soap solution into a test tube and add hydrochloric acid until flakes precipitate. What are the flakes? Write down the reaction equation. Does the precipitate dissolve in an alkaline solution? Explain your observations.

7. Place 2-3 ml of the soap solution in a test tube and add calcium chloride solution. Describe your observations. Write down the reaction equation. What property of soap is illustrated by this experiment?

8. Prove experimentally that oleic acid is an unsaturated compound.

## 5. Problems

1. Prove experimentally that polyethylene contains carbon and hydrogen.

2. Polyvinyl chloride (PVC) $(-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-)_n$ decomposes on heating

with the liberation of hydrogen chloride. Prove this experimentally.

3. Heat a small amount of a mixture of ethyl alcohol, sulphuric acid (1 : 1), and table salt in a test tube. Light the evolving gas and pay attention to the green colour of the flame. This colour is characteristic of which substance?

4. Three test tubes contain: (a) ethyl alcohol, (b) glycerol, and (c) phenol. Identify these substances chemically.

5. Place 1-2 ml of ethyl alcohol in a test tube, add an equal volume of potassium permanganate and a few drops of sulphuric acid. Heat the mixture: the colour of the solution changes. Explain. Which substance can be identified by the odour?

6. Two test tubes contain: (a) formic acid, and (b) acetic acid. Identify the formic acid chemically.

7. Identify experimentally: (a) an unsaturated hydrocarbon, (b) a polyhydric alcohol, (c) an aldehyde, and (d) a carboxylic acid.

8. Identify by specific reactions: (a) straight-run petrol, (b) cracked petrol; (c) solutions of acetic acid, phenol, and ethyl alcohol.

## 6. Preparing Ethyl Acetate

Write down the equation for the reaction by which an ester is obtained from acetic acid and ethyl alcohol. Use the apparatus shown in Fig. 61, slightly modified as instructed below.

Place 10-12 ml of a mixture of ethyl alcohol, acetic acid, and sulphuric acid into a flask and connect an air- or water-cooled condenser. Lower the other end of the condenser into a receptacle placed in a mixture of water and ice. Heat the flask on a water bath or on a wire gauze over a burner (Caution!). When a sufficient amount of the ester has been collected, and the distillation rate slows down, discontinue the experiment.

In order to isolate the ester from the alcohol and acid, add water and shake the mixture. Separate the mixture in a separating funnel.

## 7. Problems

1. Three test tubes contain solutions of: (a) glycerol, (b) aldehyde, and (c) glucose. Identify them by using the same reagents.

2. A lubricating oil obtained from petroleum and a vegetable oil are placed in separate test tubes. Identify them chemically.

3. Prepare: (a) an ether, (b) an aldehyde, (c) an acid, and (d) an ester from ethyl alcohol.

4. Prove experimentally that common sugar contains carbon.

5. Prove experimentally that: (a) potato and wheat bread contain starch, and that (b) a ripe apple contains glucose.

6. Using specific reactions identify (a) starch, sugar, and glucose, (b) glycerol, soap, and starch (solutions).

## 8. Identifying Plastics

Obtain specimens of various plastics from your teacher and identify each of them by the following signs.

Polyethylene. A translucent and elastic material oily to the touch. Softens on heating. Fibres can be drawn from its melt. Burns with a bluish flame to give the odour of molten paraffin. Continues burning when removed from the flame.

Polyvinyl Chloride. Elastic or hard material. Softens quickly on heating; decomposes with liberation of hydrogen chloride. Burns with a smoky flame; does not burn outside the flame.

Polystyrene $(-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-)_n$. It can be either translucent or opaque; often brittle. Softens on heating; fibres can be drawn from its melt. Burns with a smoky flame to give the odour of styrene; continues burning outside the flame.

Polymethyl Methacrylate $(-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-)_n$. This is normally a translucent material; may be coloured. When heated it softens; fibres cannot be drawn from its melt. Burns with a yellowish flame with blue margins and with specific crackling sounds to give the odour of the ether.

Phenolformaldehyde Resin. This is a material of dark shades (from brown to black). Decomposes on heating. Burns with difficulty to give the odour of phenol; stops burning when removed from the flame.

## 9. Identification of Fibres

Obtain samples of some fibres and identify them by the following signs.

Cotton. Burns quickly to give the odour of burnt paper. Leaves grey ash after combustion.

Wool and Natural Silk. Burn slowly to give the odour of burnt feathers. A black ball is formed after combustion which can be crushed to powder.

Acetate Fibre. Burns quickly to form a dark-brown ball of a sintered mass. As distinct from other fibres, acetate dissolves in acetone.

Nylon 6. Softens on heating and then melts. Fibres can be drawn from its melt. Burns to give an unpleasant odour.

# Appendix

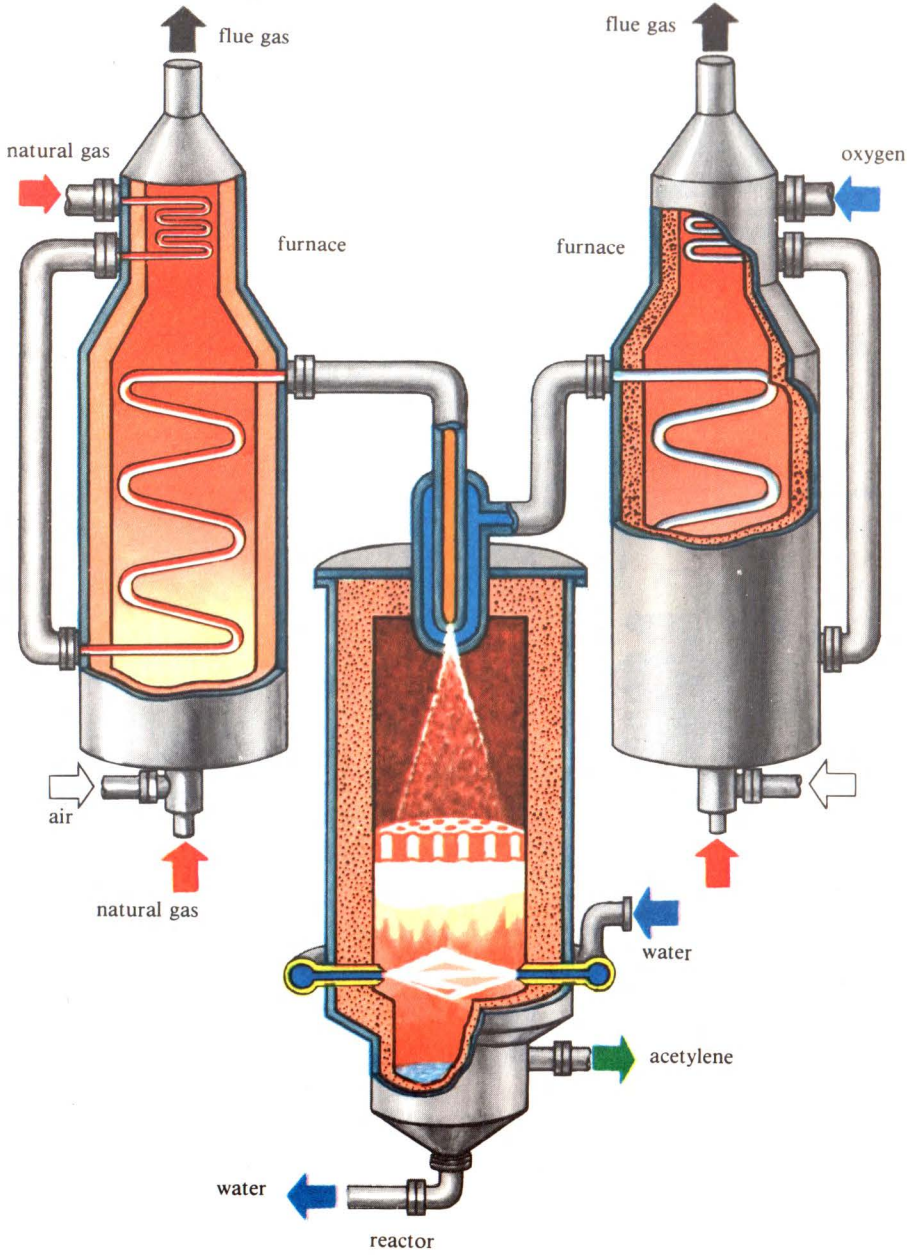


Fig. I. Industrial plant for preparing acetylene from methane

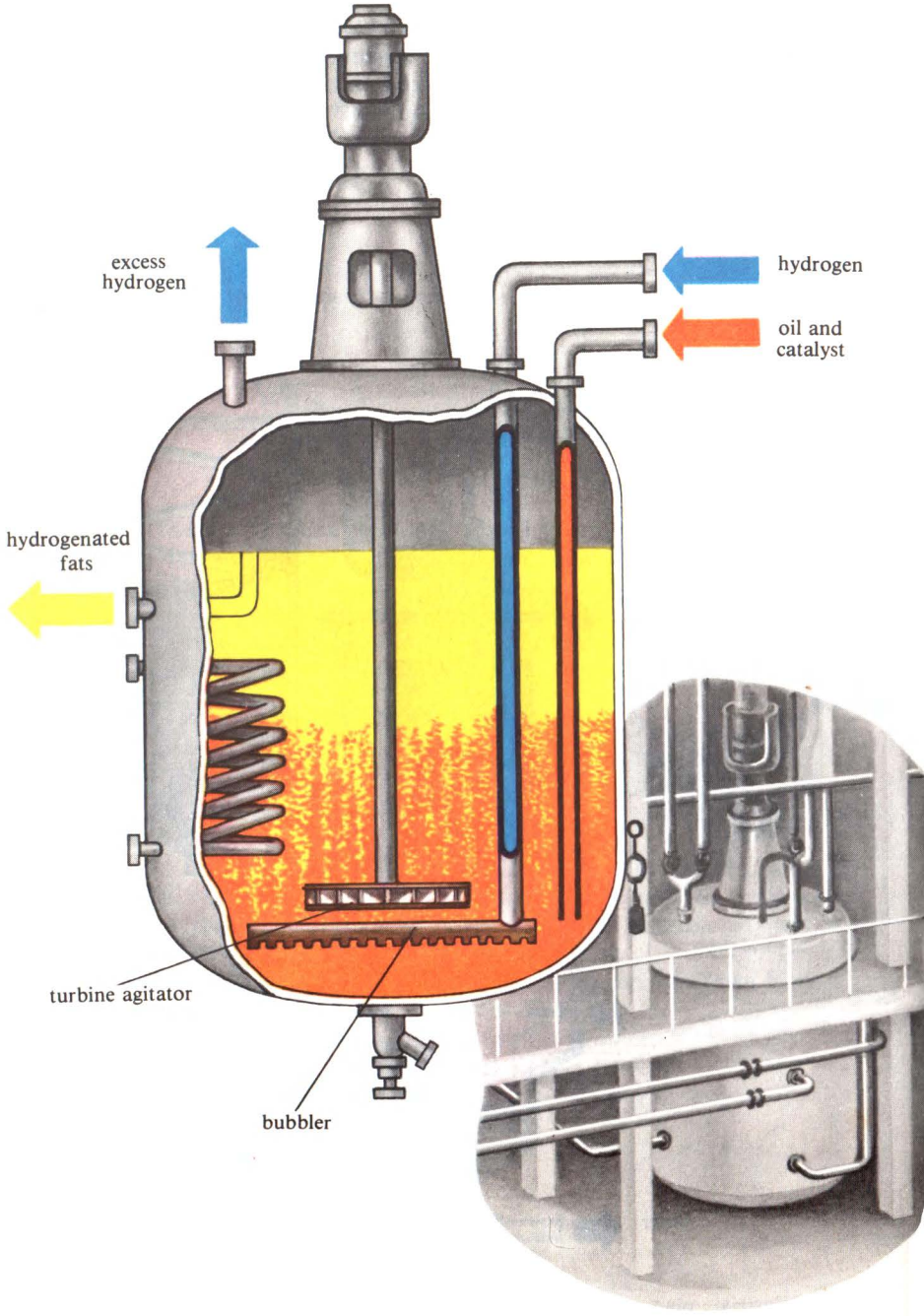


Fig. II. Hydrogenation of fats

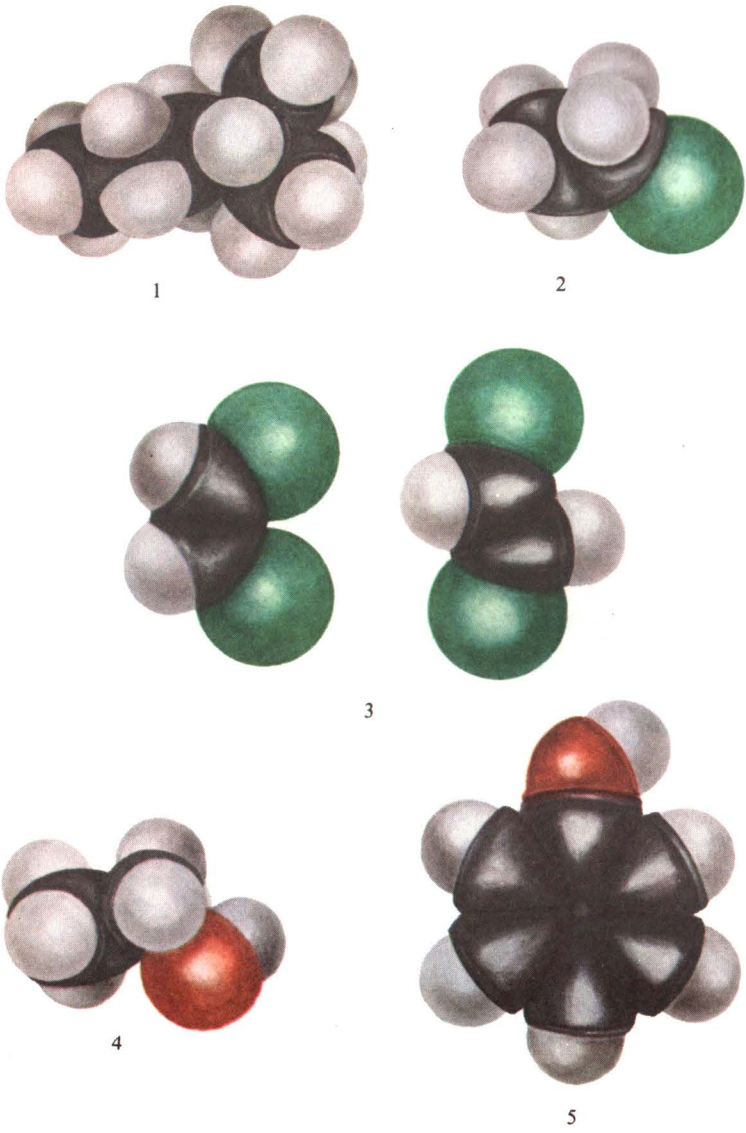


Fig. III. Model of molecules of:

*1* – isohexane; *2* – ethyl chloride; *3* – *cis*- and *trans*-isomers of dichloroethylene; *4* – ethyl alcohol; *5* – phenol

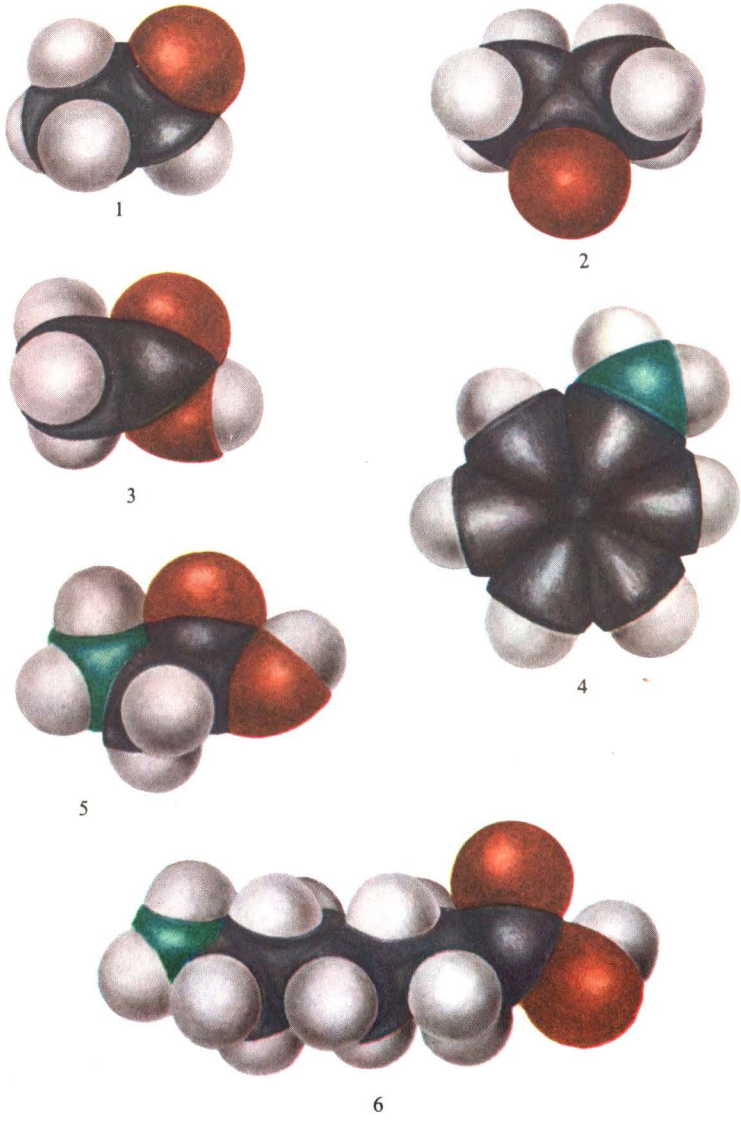


Fig. IV. Models of molecules of:

*1* – acetaldehyde; *2* – acetone; *3* – acetic acid; *4* – aniline; *5* – aminoacetic acid; *6* – aminocaproic acid